Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced synthesis of α-trifluoromethylated ketones through the oxidative trifluoromethylation of styrenes using CF_3SO_2Na as trifluoromethyl reagent without external photoredox catalyst

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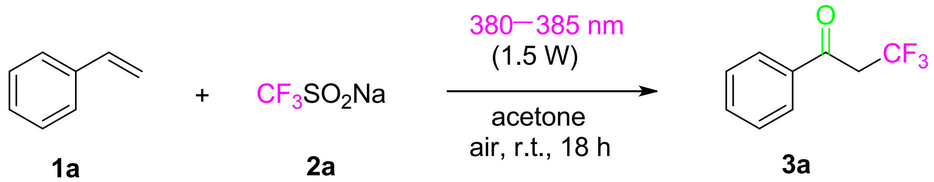
1. General consideration

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

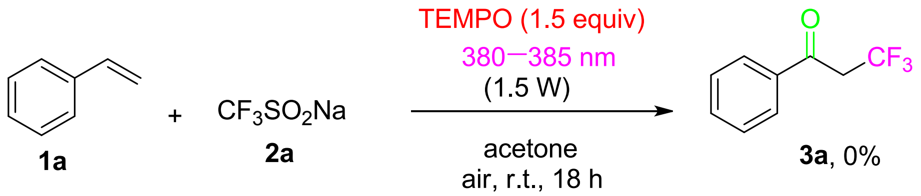
2. Representative procedure for the model reaction



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with styrene (**1a**, 0.20 mmol), sodium trifluoromethanesulfinate (**2a**, 0.40 mmol) and acetone (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 1.5 W) irradiation at room temperature in air with stirring for 18 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 50:1) to give the desired product **3a**.

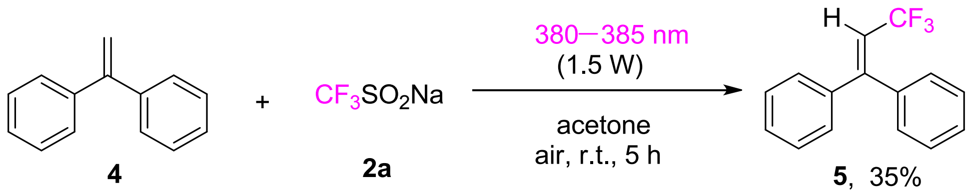
3. Mechanism investigation

3.1 Radical inhibition experiment



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with styrene (**1a**, 0.20 mmol), sodium trifluoromethanesulfinate (**2a**, 0.40 mmol), TEMPO (0.30 mmol) and acetone (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 1.5 W) irradiation in air at room temperature with stirring for 18 h. The reaction was completely inhibited, indicating a radical pathway involved in the reaction.

3.2 Radical capture experiment



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with sodium trifluoromethanesulfinate (**2a**, 0.40 mmol), 1,1-diphenylethylene (**4**, 0.20 mmol) and acetone (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 1.5 W) irradiation in air at room temperature with stirring for 5 h. The adduct **5** was given 35% isolated yield, and was determined by the NMR analysis.

3.3 Determination of electron spin resonance (ESR)

3.3.1 Determination of superoxide radicals

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) was used to capture $O_2^{\bullet-}$ (g =

2.0060). There was no signal when DMPO was added into air-saturated acetone solution of styrene (**1a**) without light (Figure S1a). Irradiation of air-saturated acetone of DMPO with **1a** with LED (380–385 nm, 1.5 W) resulted in the formation of a characteristic signal of $O_2^{\bullet-}$ with DMPO (Figure S1b), indicating the formation of $O_2^{\bullet-}$ in the reaction.

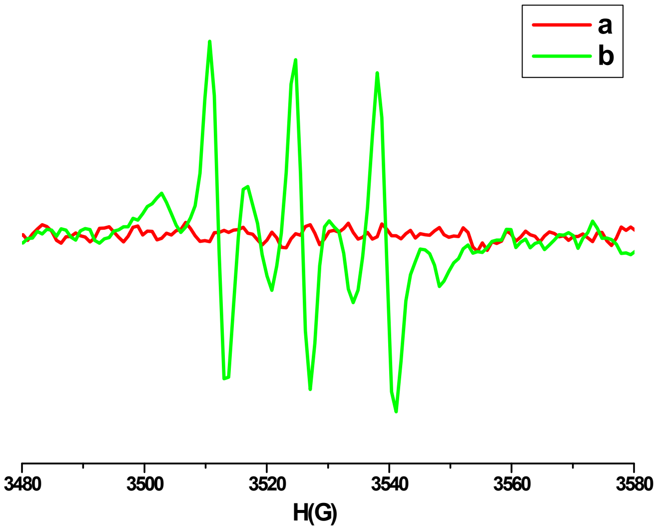


Figure S1. Electron spin resonance (ESR) spectra of $O_2^{\bullet-}$ with DMPO

(**a**) A solution of **1a** with DMPO (0.20 mol/L) in air-saturated acetone without light irradiation.

(**b**) A solution of **1a** with DMPO (0.2 mol/L) in air-saturated acetone under LED (380-385 nm) irradiation for 180 s.

3.3.2 Determination of singlet oxygen species

For further exploration of the active species of singlet oxygen involved during the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) was used to trap $^1O_2$ (g = 2.0065). Irradiation of air-saturated acetone solution of styrene (**1a**) with TEMP under LED (380–385 nm, 1.5 W) irradiation resulted in the formation of a characteristic signal $^1O_2$ adduct with TEMP (Figure S2). The characteristic signal of $^1O_2$ was collected (Figure S2), implying that $^1O_2$ was present in the reaction.

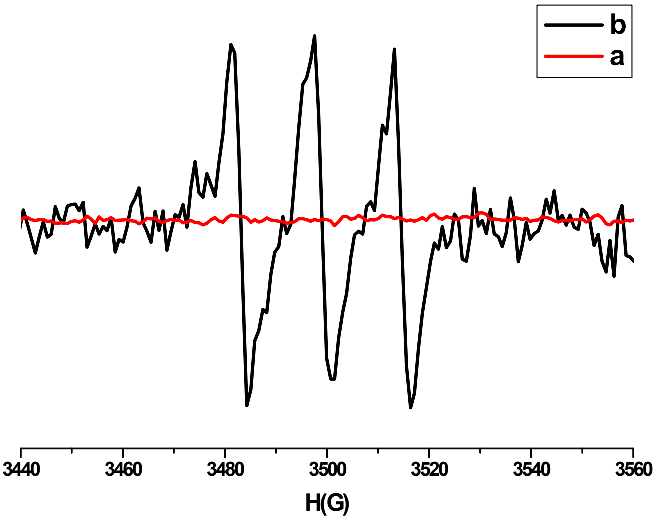


Figure S2. Electron spin resonance (ESR) spectra of $^1O_2$ adduct with TEMP

(a) A solution of styrene (**1a**) with TEMP (0.20 mol/L) in air-saturated acetone without light irradiation.

(b) A solution of styrene (**1a**) with TEMP (0.20 mol/L) in air-saturated acetone under LED (380–385 nm, 1.5 W) irradiation for 180 s.

3.4 Absorption spectra of acetone and products

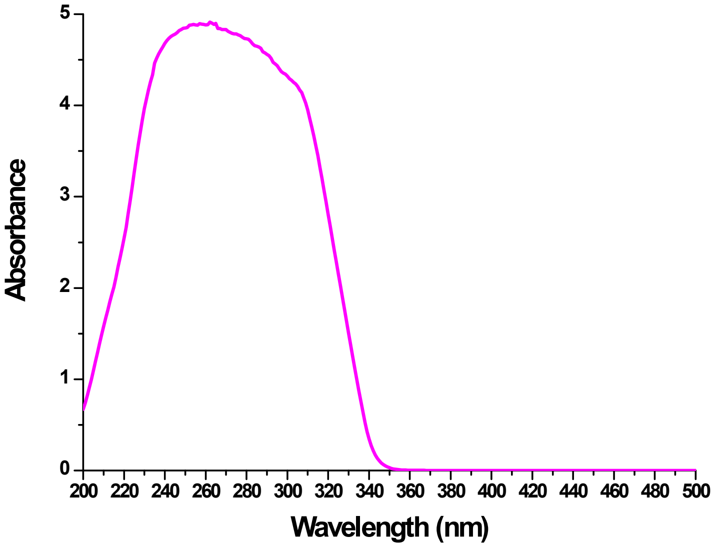


Figure S3. Absorption spectra of acetone

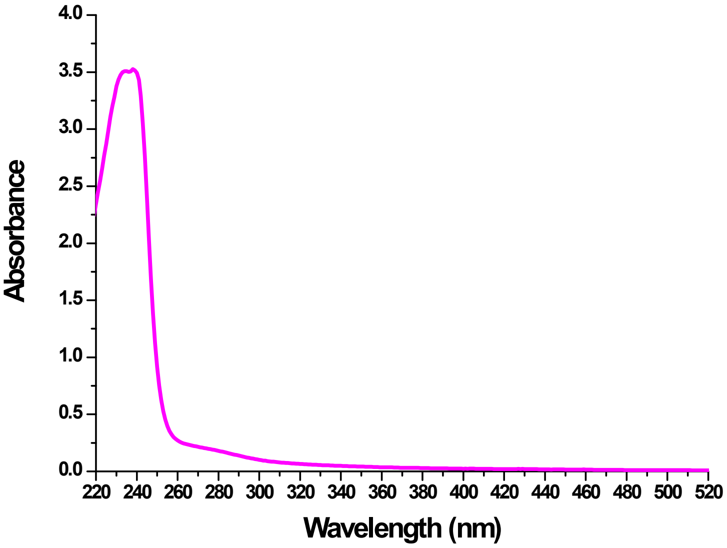


Figure S4. Absorption spectra of sodium trifluoromethanesulfinate (**2a**) in water

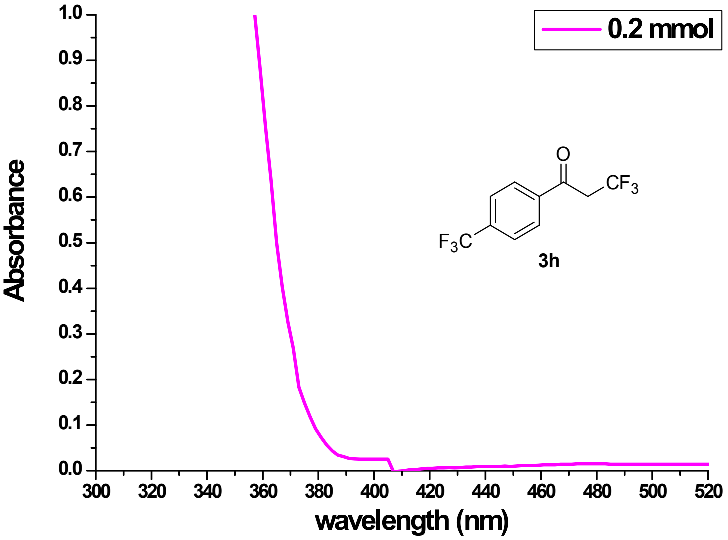


Figure S5. Absorption spectra of 3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl) propan-1-one (**3h**) in acetone (3.0 mL)

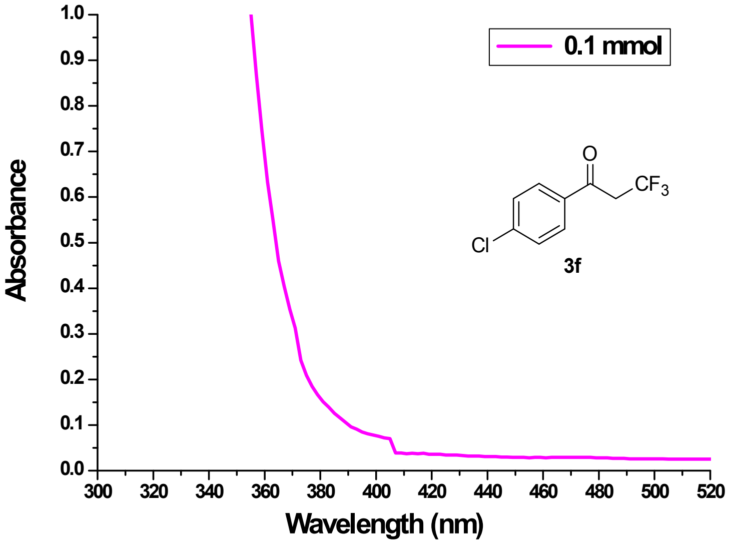
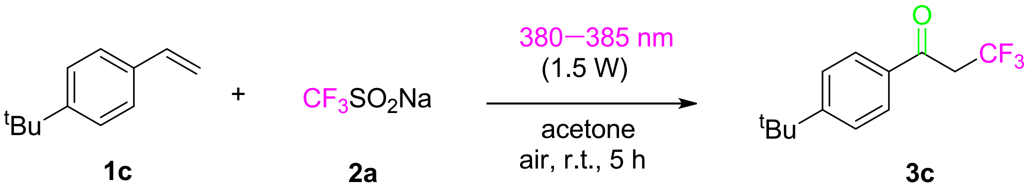


Figure S6. Absorption spectra of 1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one (**3f**) in acetone (3.0 mL)

3.4 Light/Dark experiments

In order to illustrate the oxidative trifluoromethylation by self-sustaining in an autocatalytic manner, the light/dark experiments were conducted, shown in Figure S8. A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 1-(*tert*-butyl)-4-vinylbenzene (**1c**, 0.20 mmol), sodium trifluoromethanesulfinate (**2a**, 0.40 mmol) and acetone (2.0 mL). The reaction vessel was exposed to LED (380–385 nm, 1.5 W) irradiation in air at room temperature with stirring for 5.5 h, then stirring for 1 h without irradiation. The following product yields on the irradiation with LED (380–385 nm, 1.5 W) in air at room temperature for a certain time, and without irradiation for a certain time were also presented in the Figure S7.



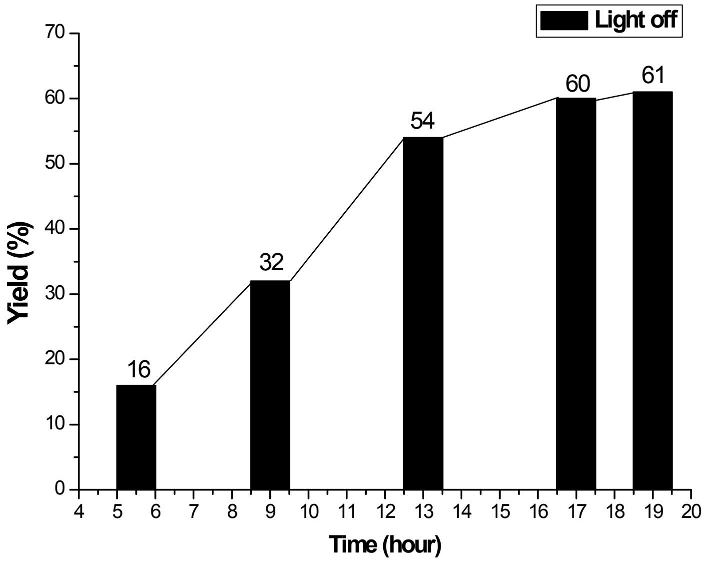
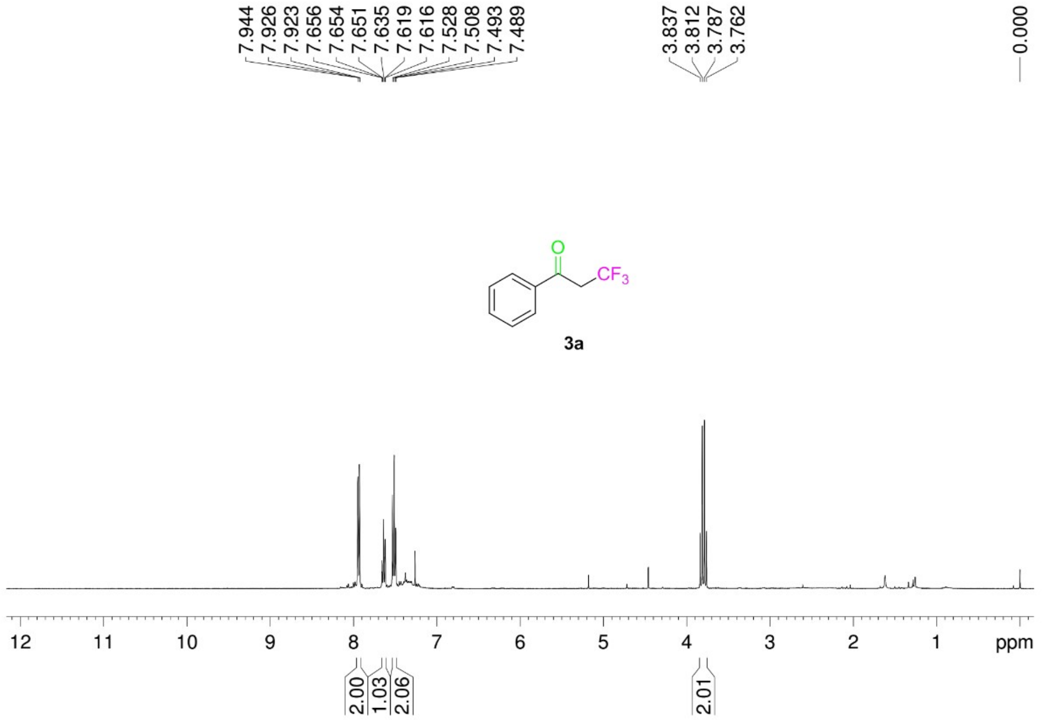
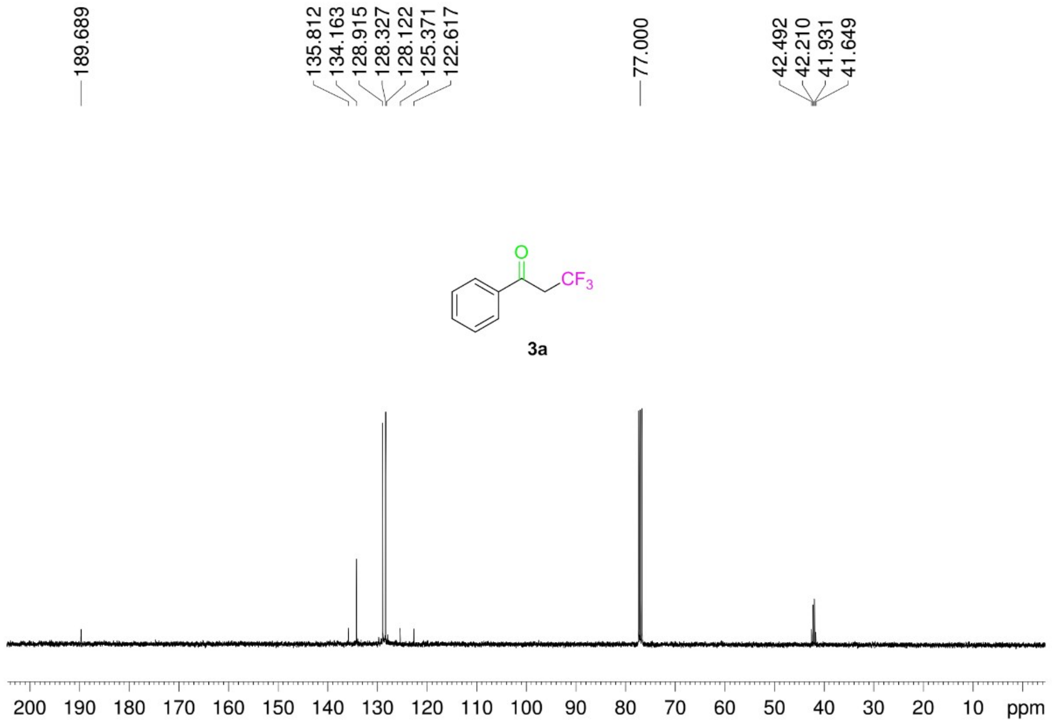
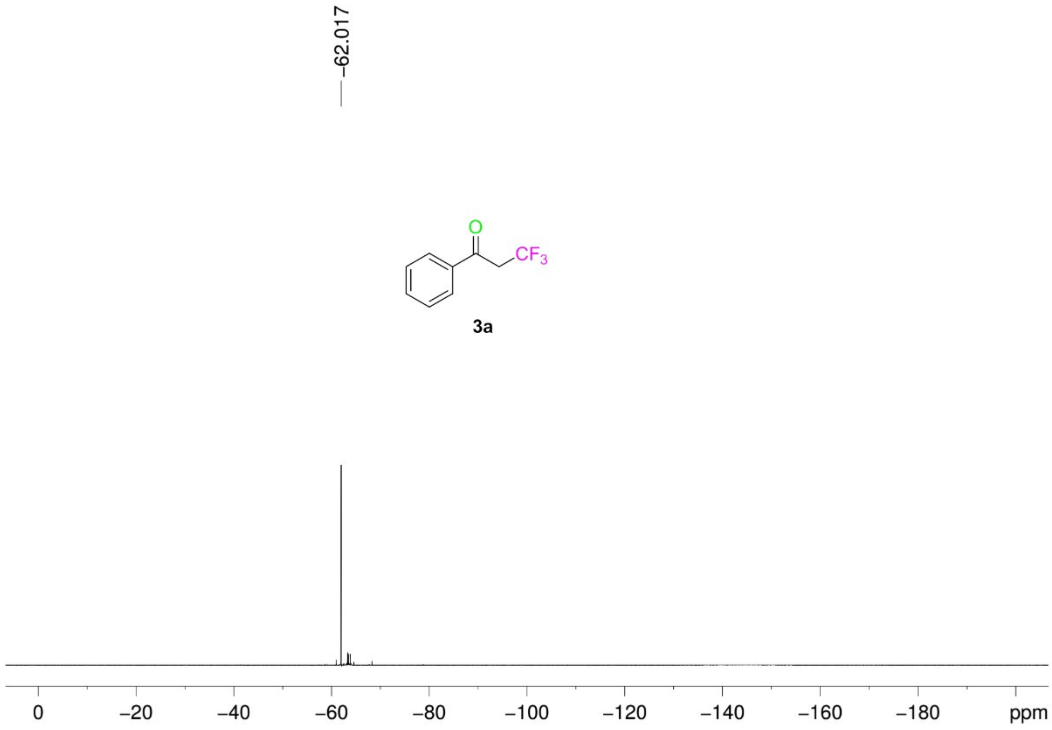


Figure S7. Light/dark experiments

4. ^{1}H, ^{13}C and ^{19}F NMR spectra of the products



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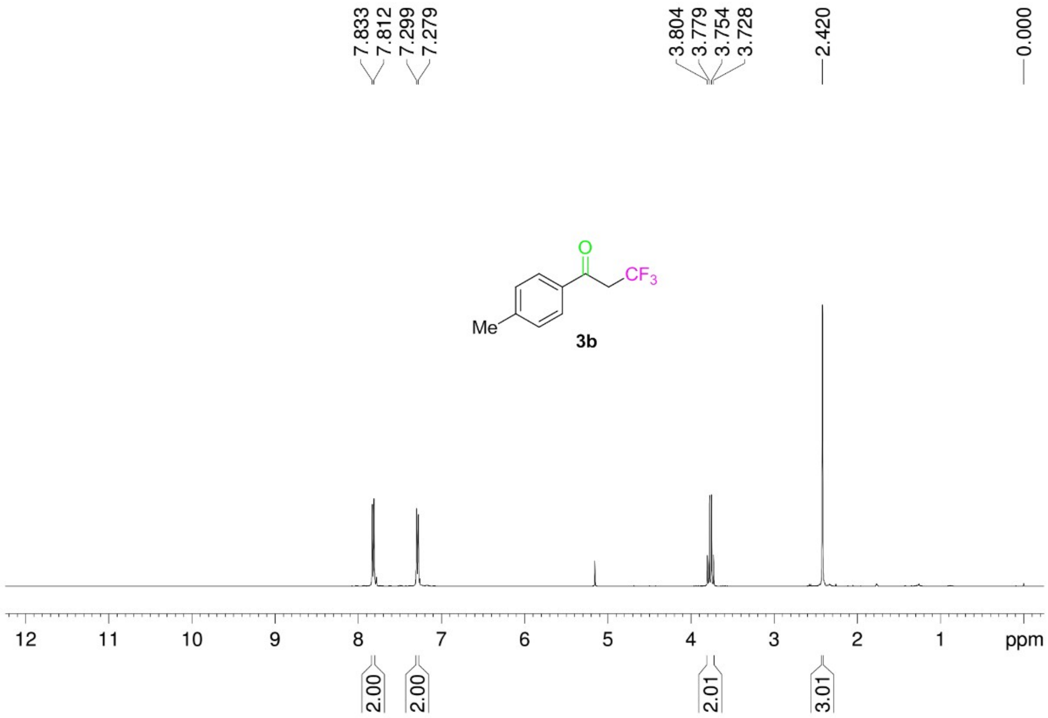
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2.00
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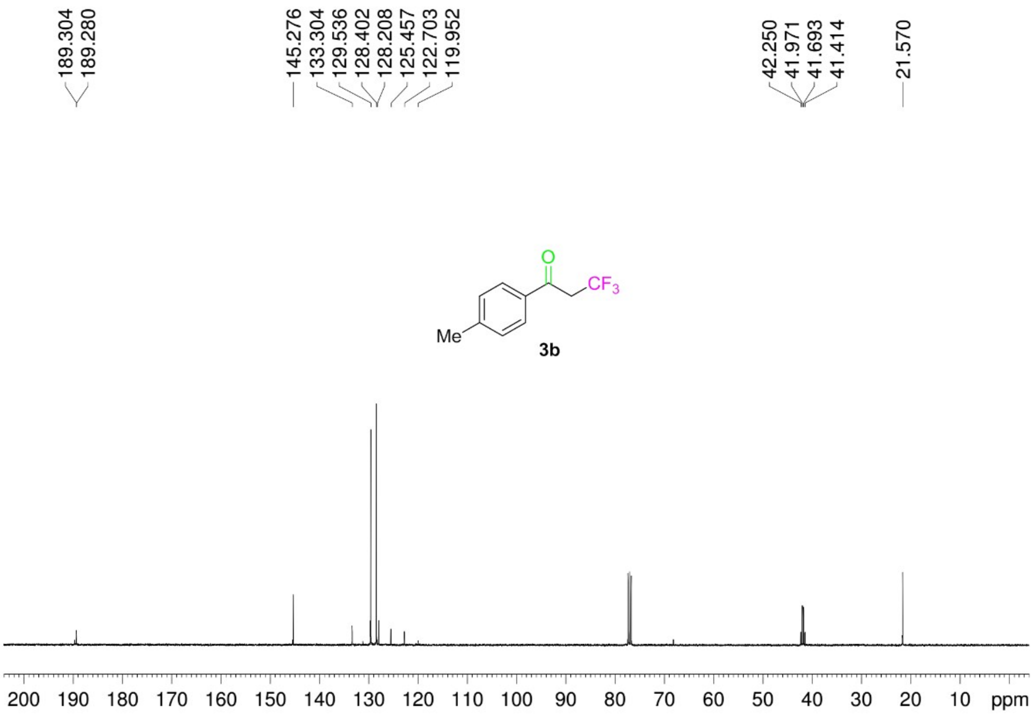
3.01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41.693
41.414
21.570
O
CF3
Me
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


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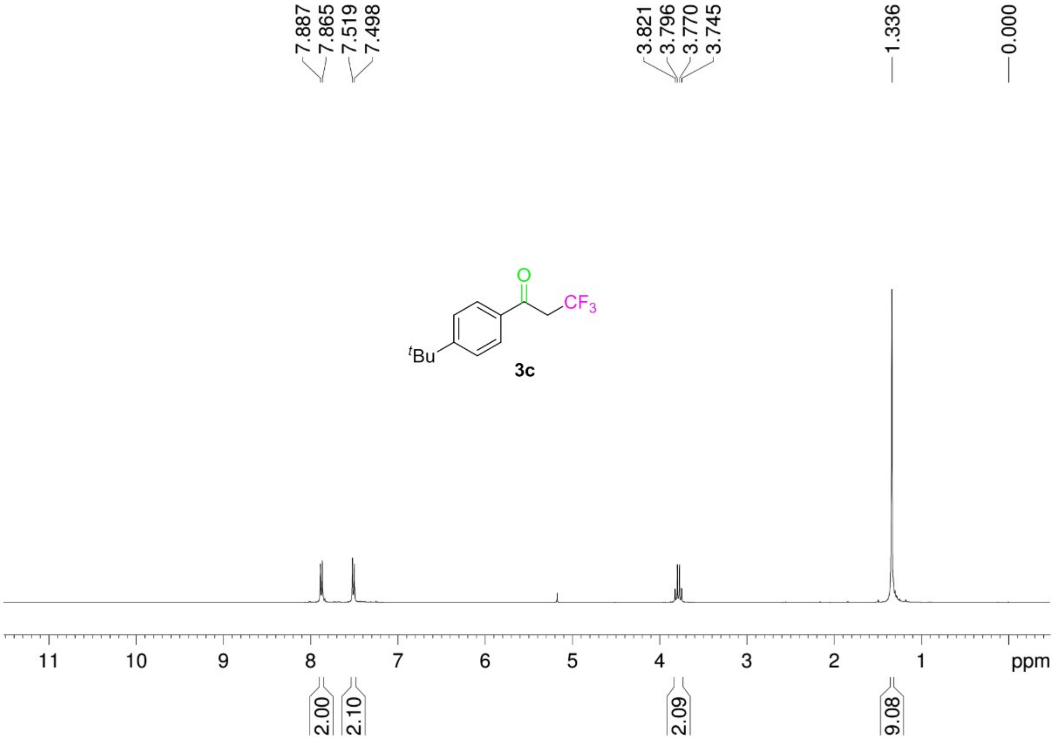
CF3
Me
3b
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 ppm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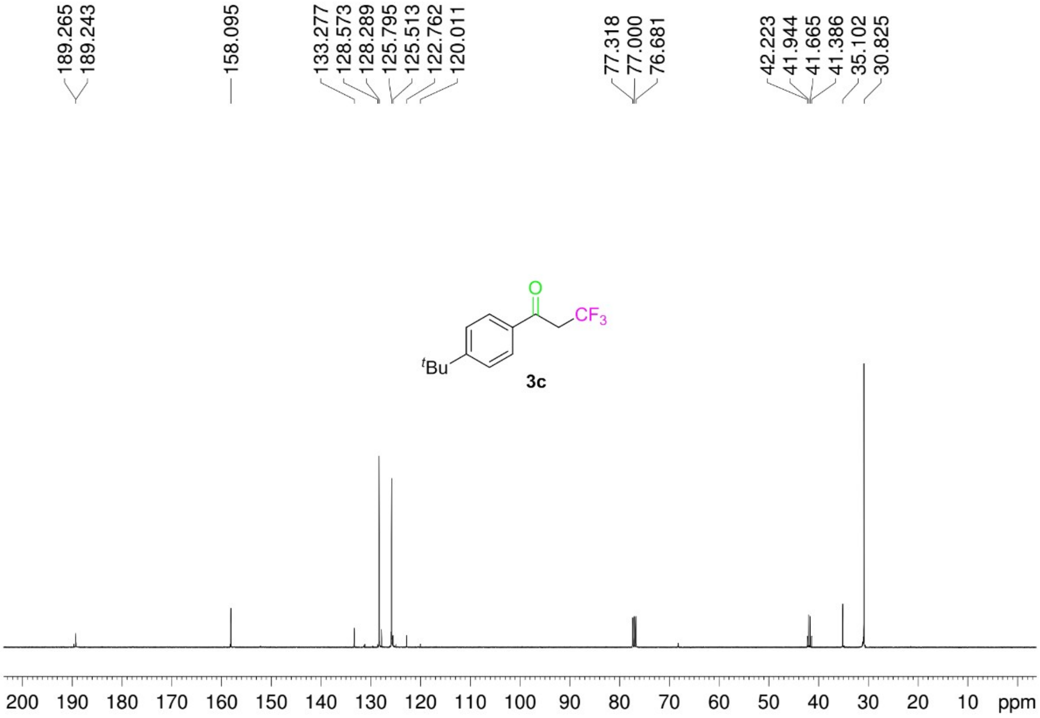
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tBu
3c
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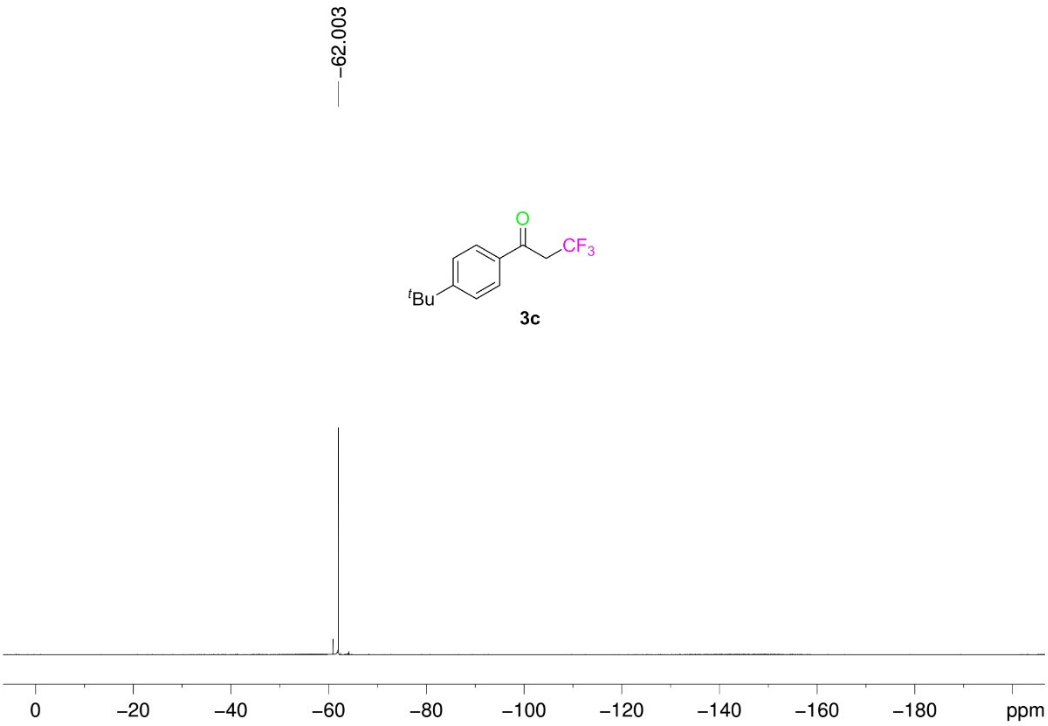
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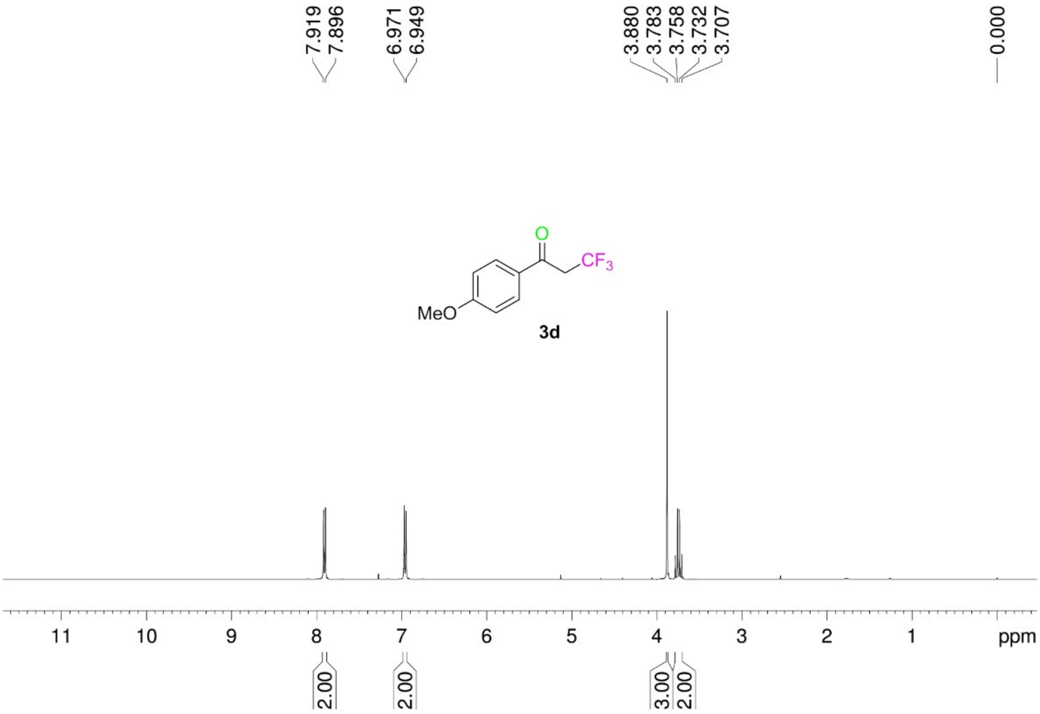
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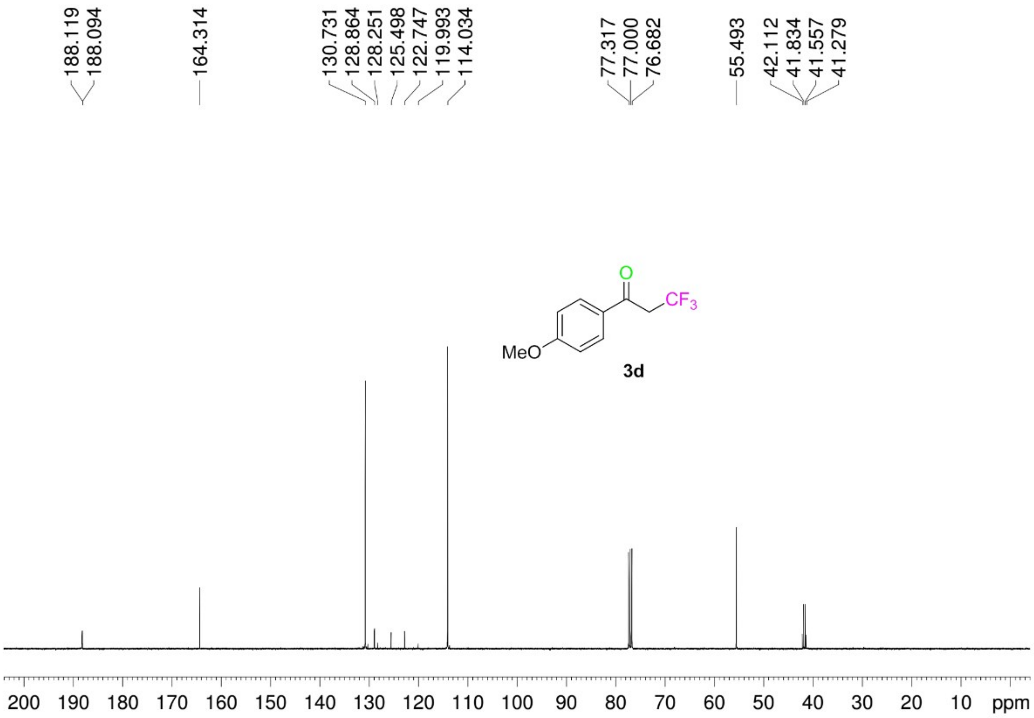
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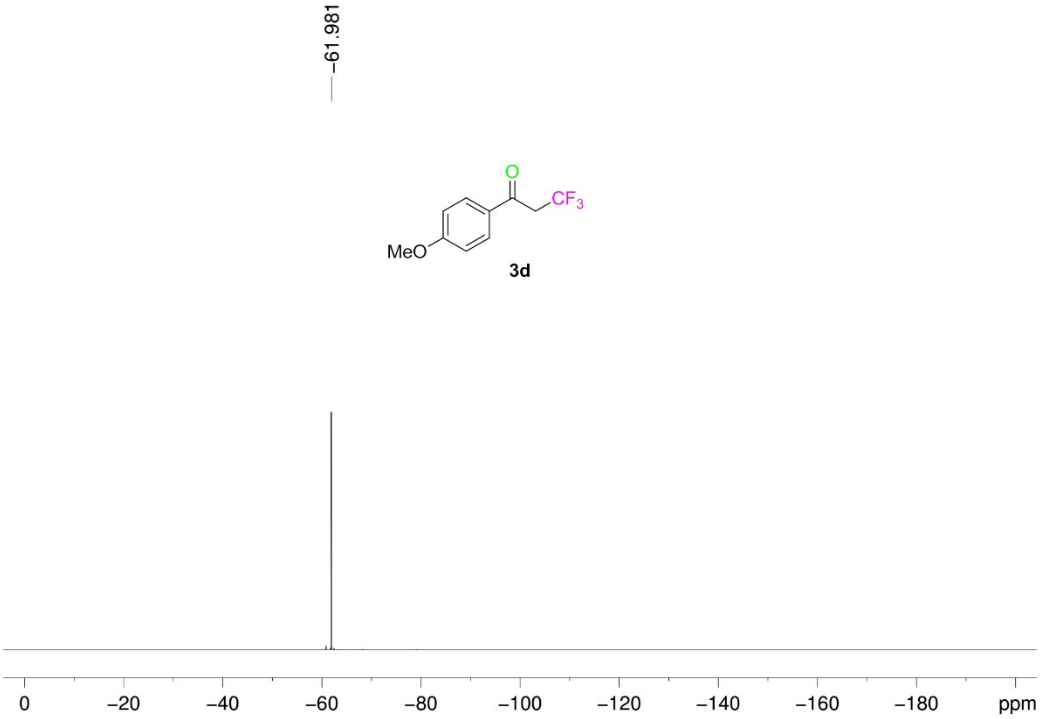
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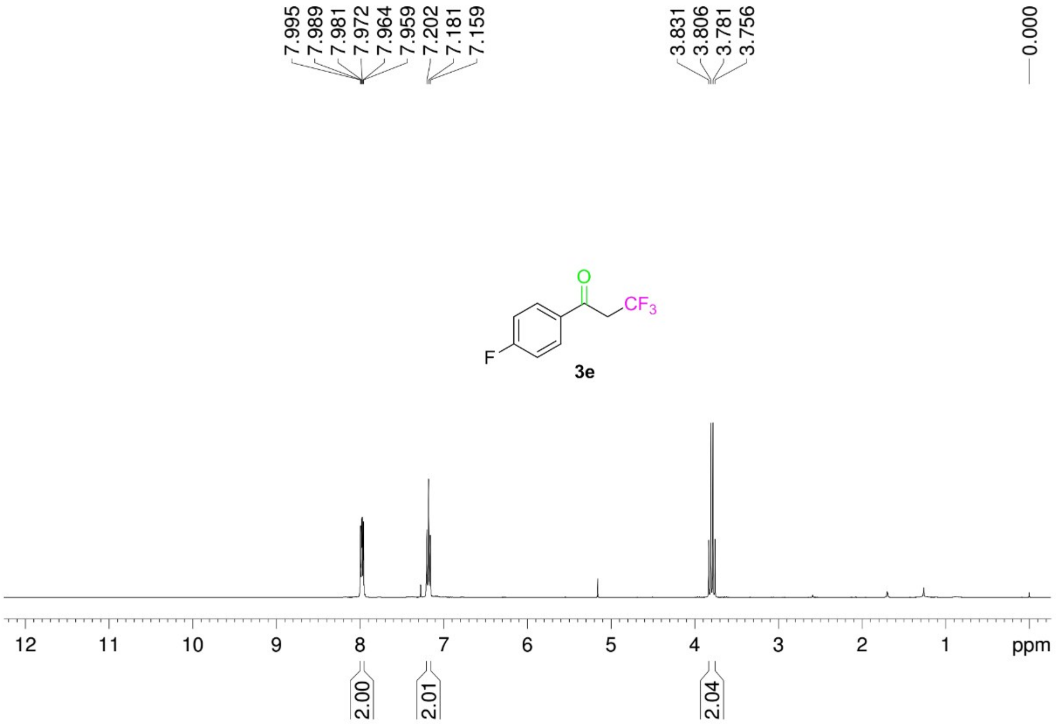
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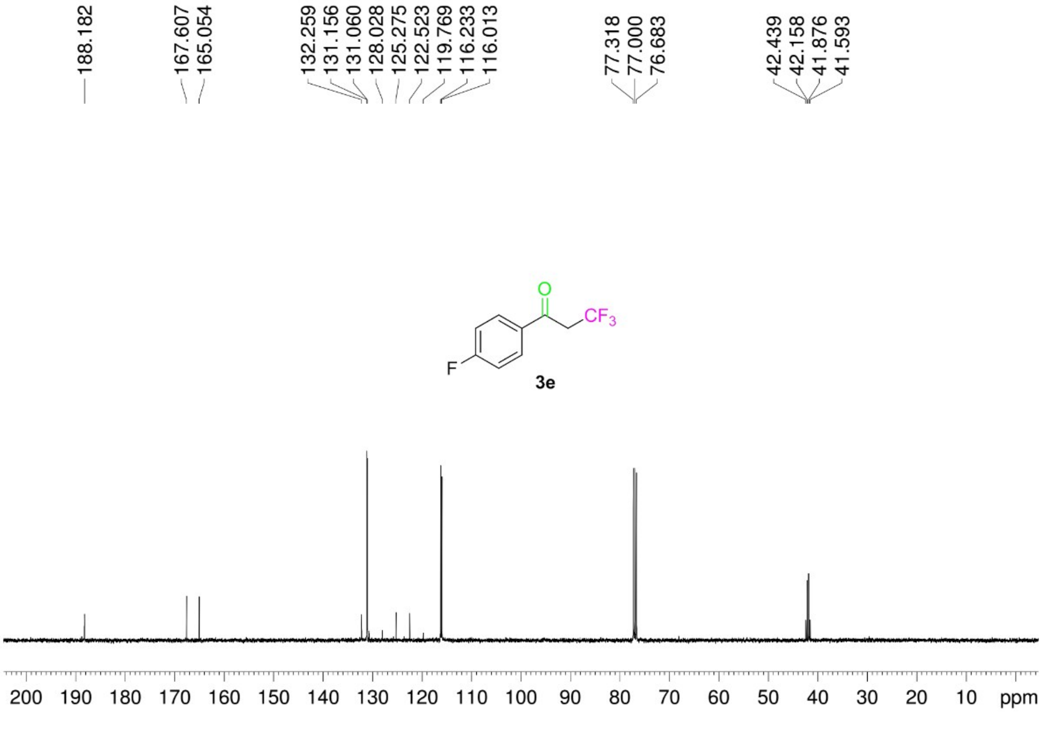
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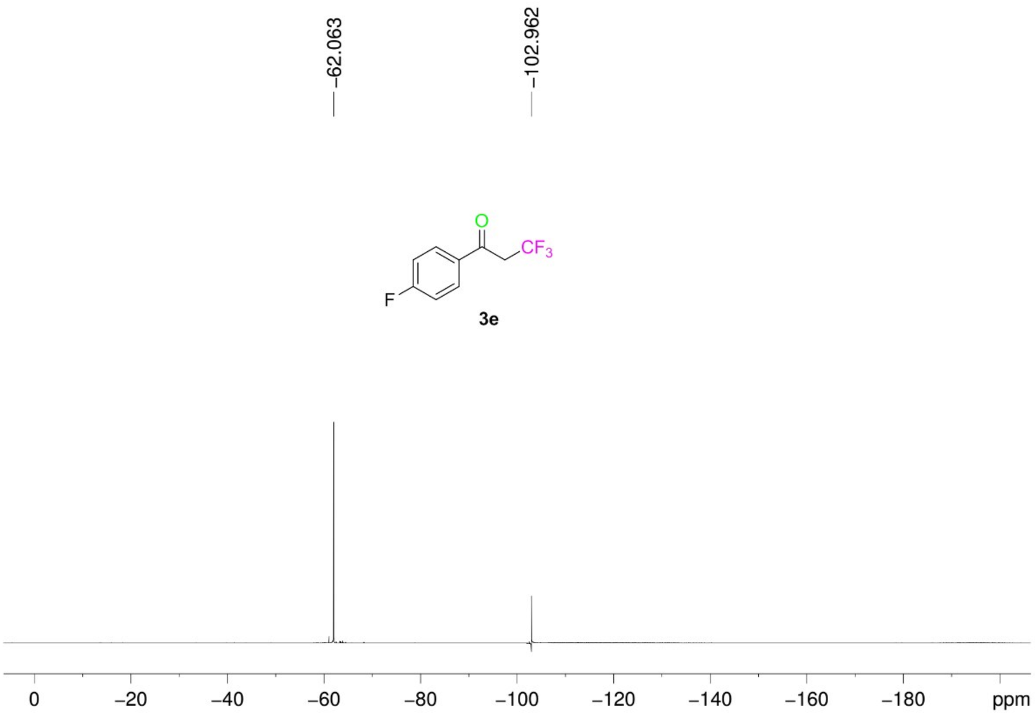
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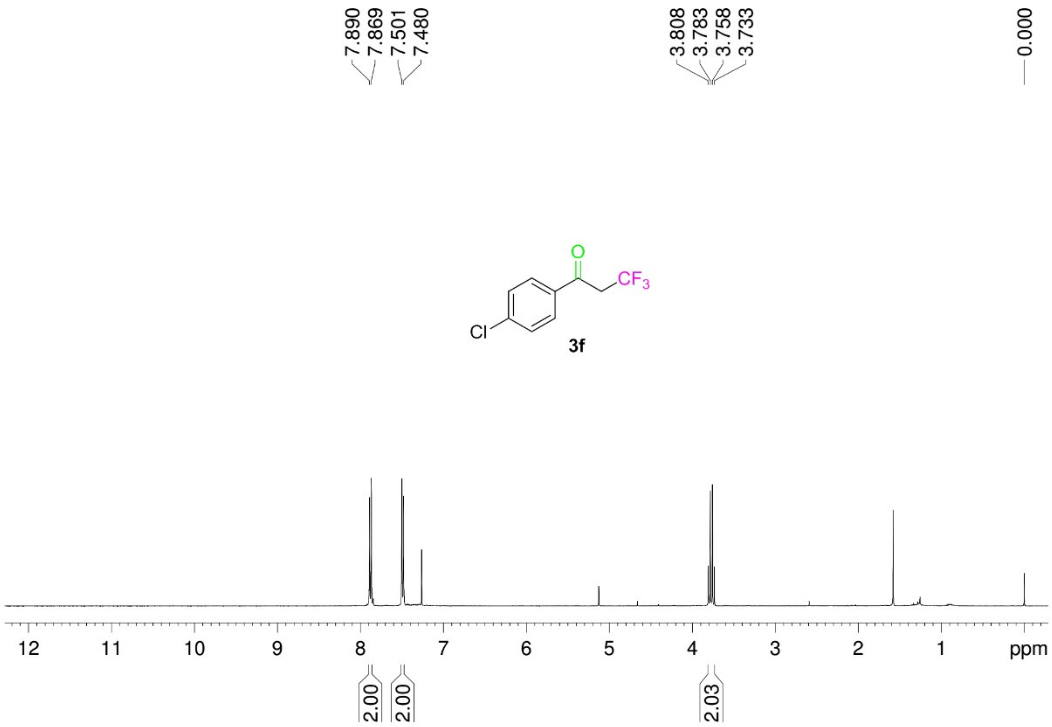
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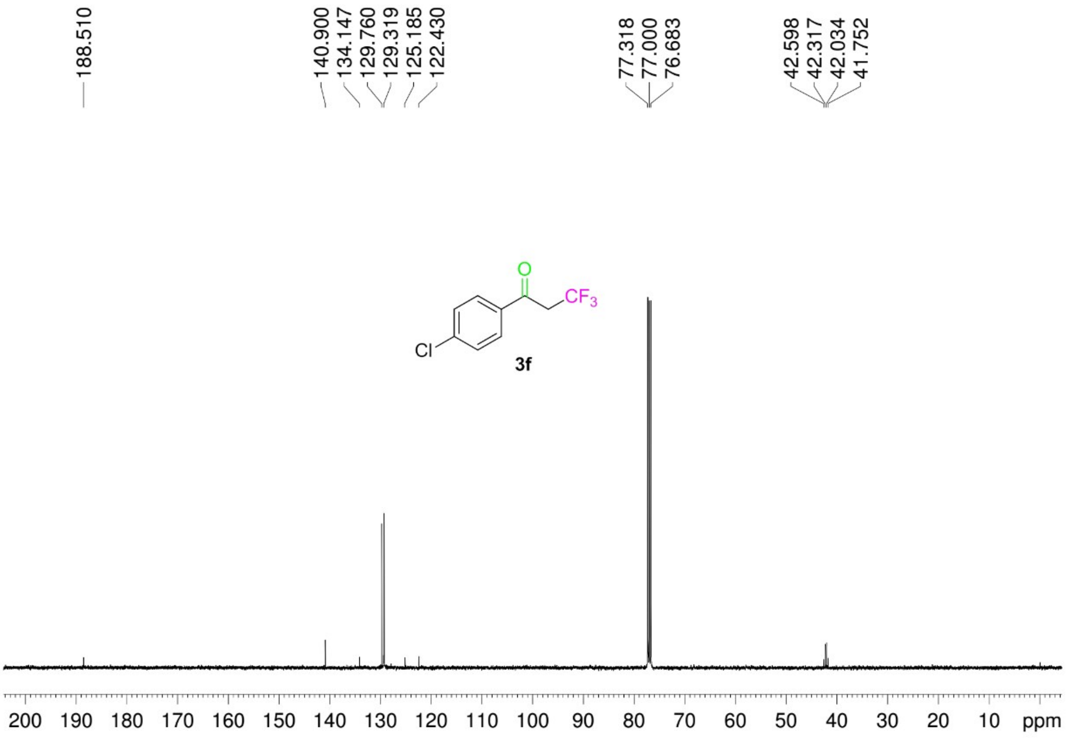
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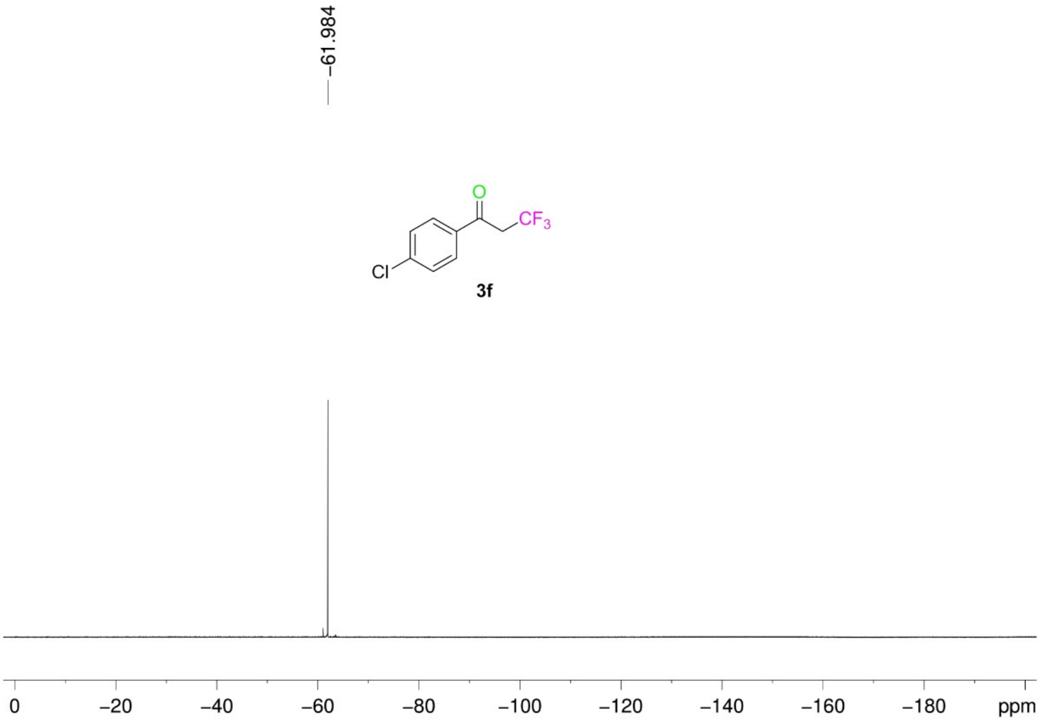
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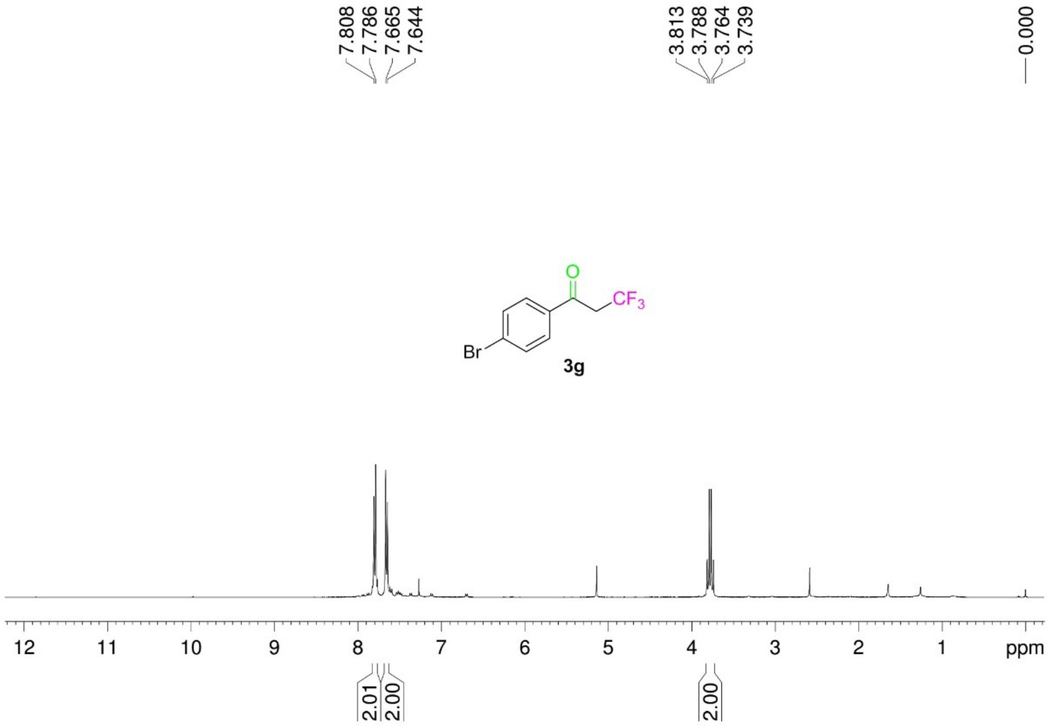
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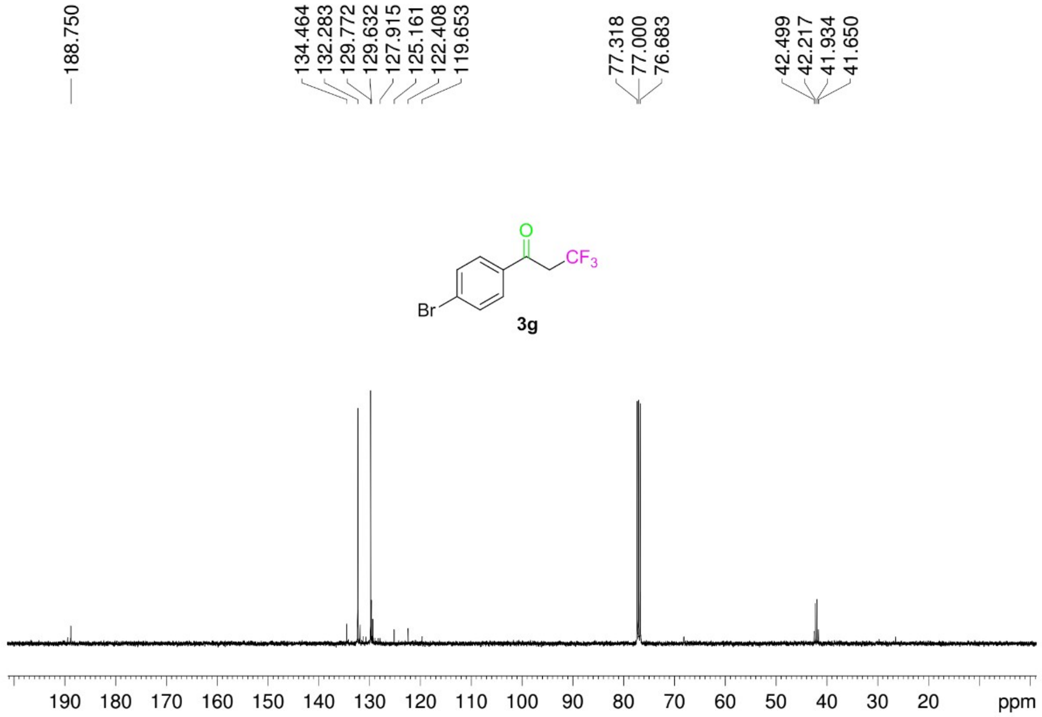
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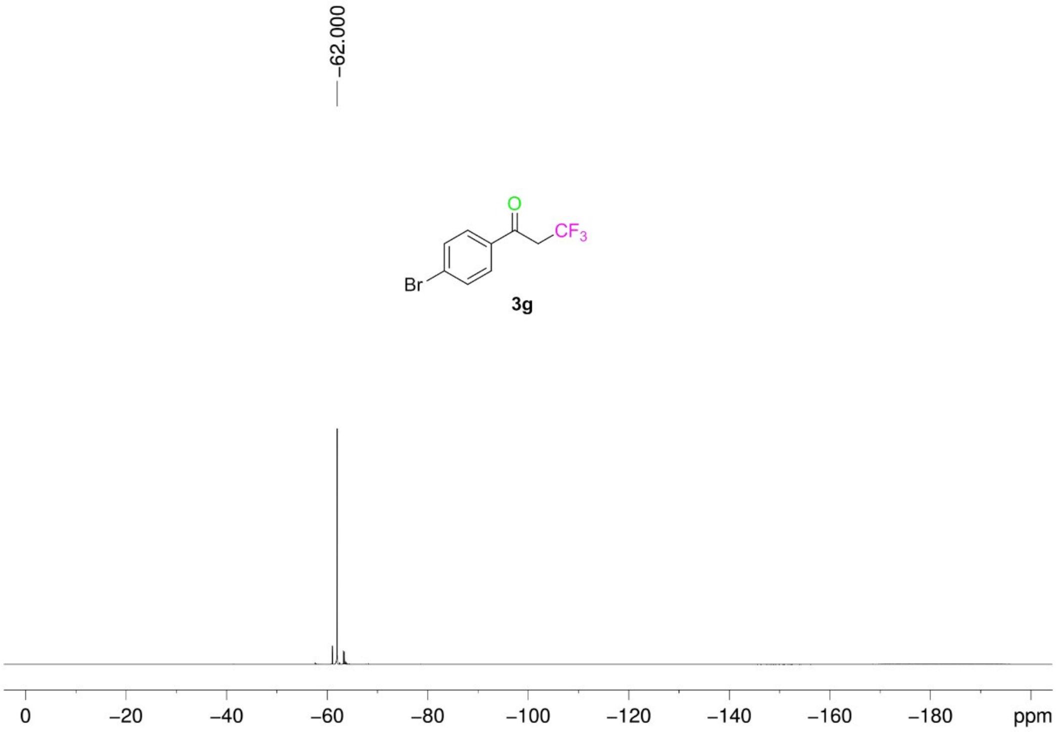
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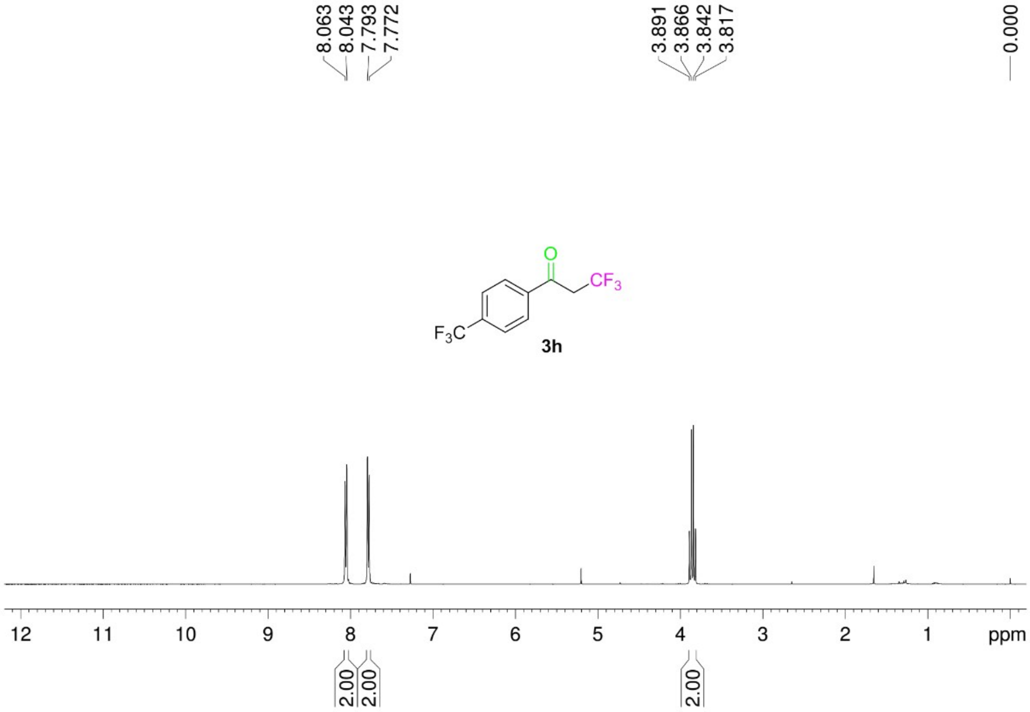
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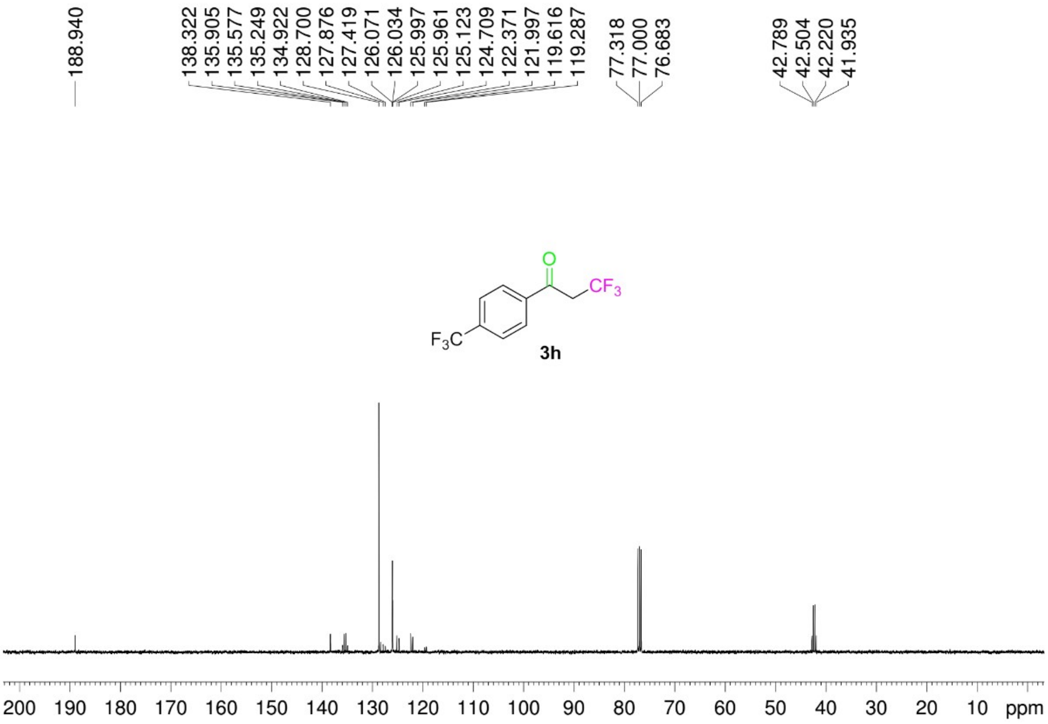
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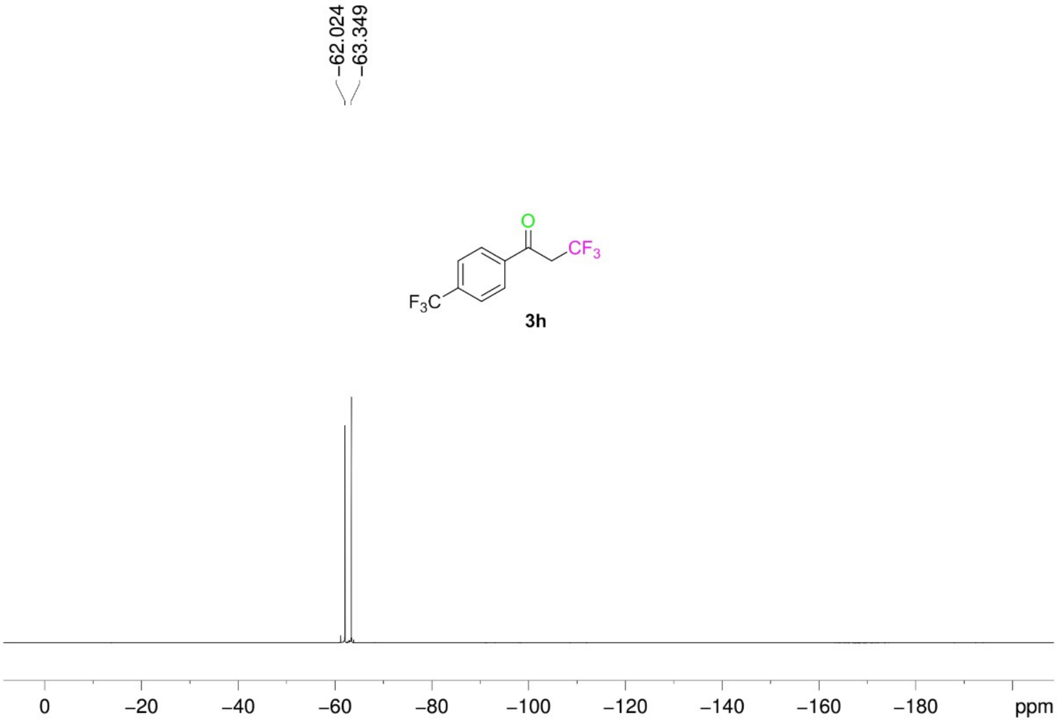
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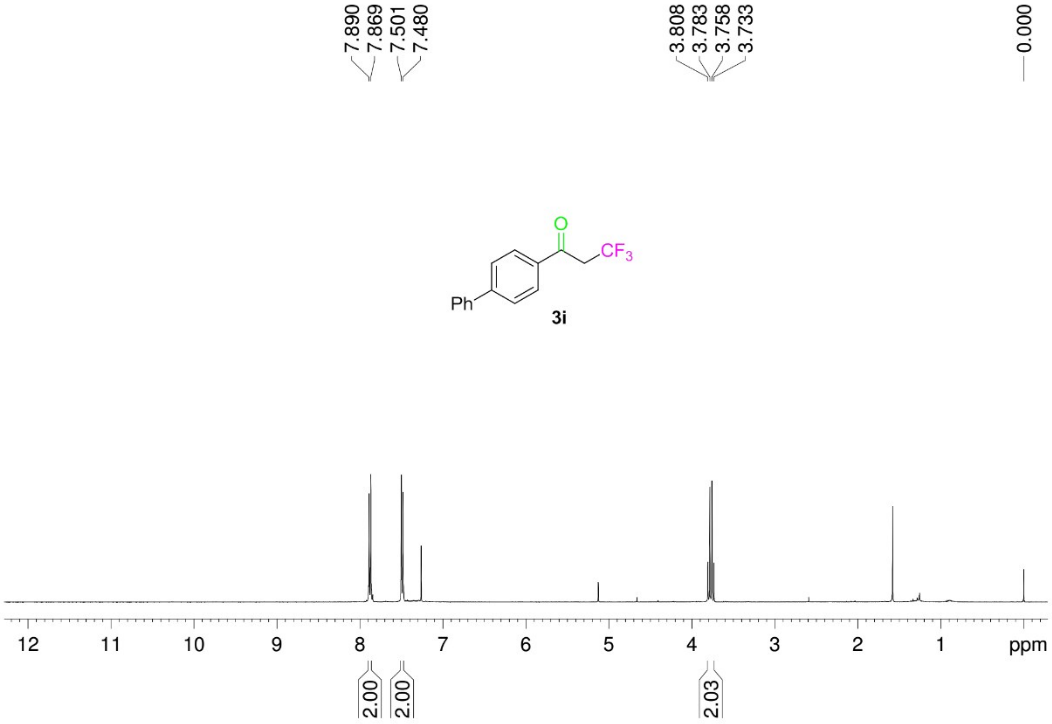
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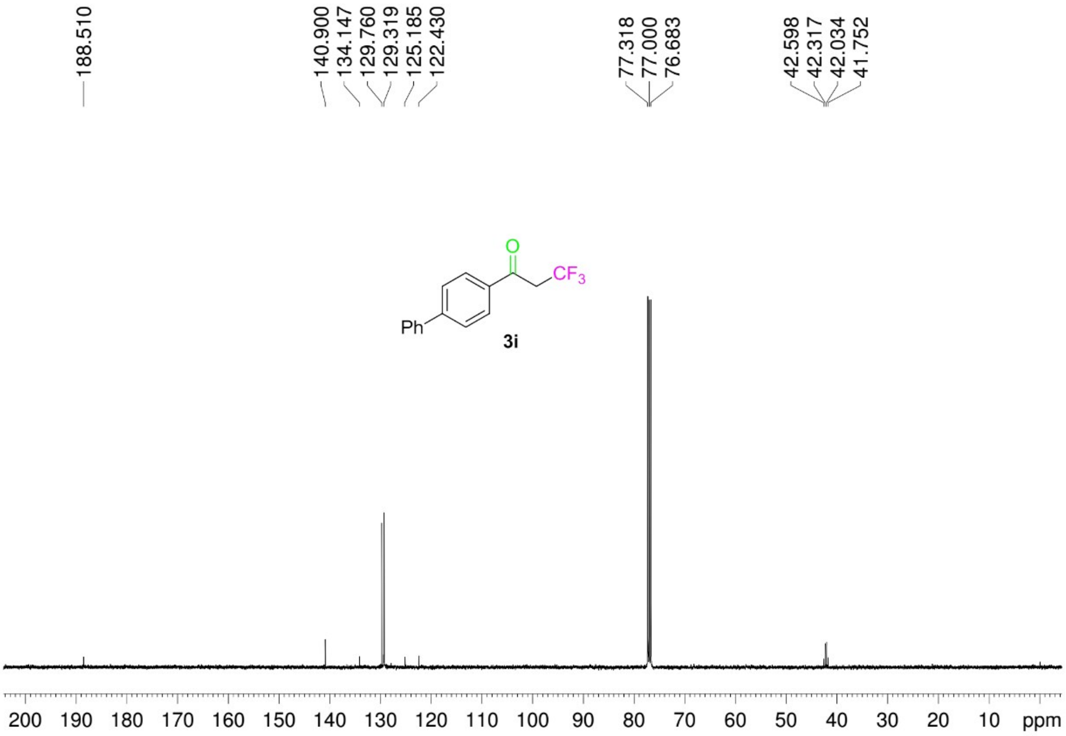
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O
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3i
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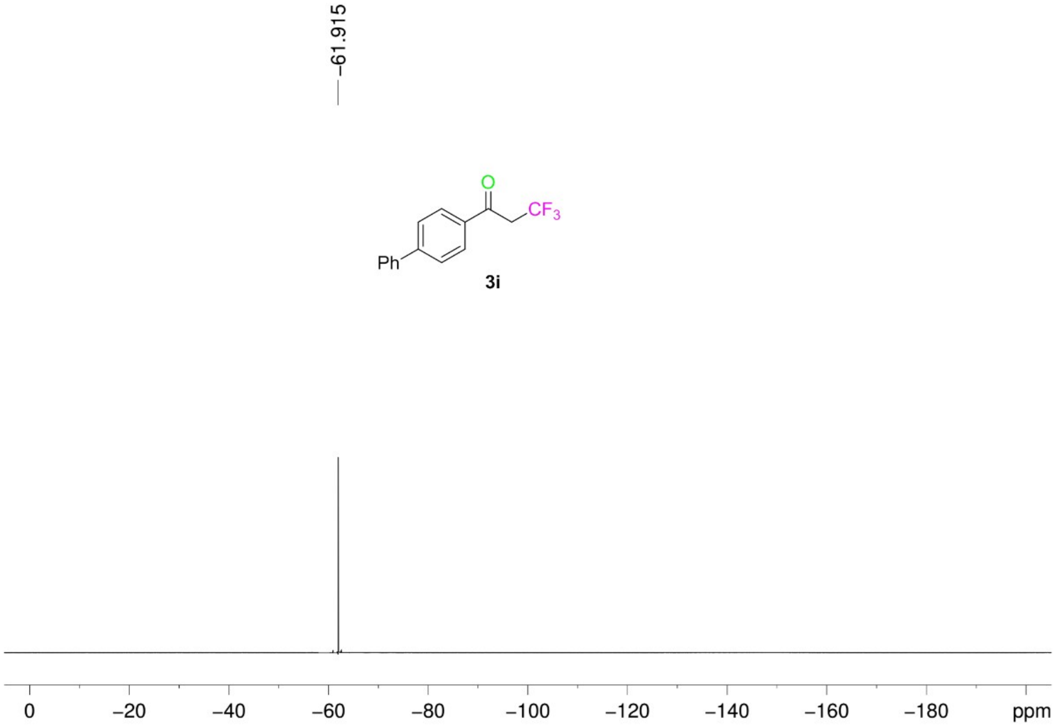
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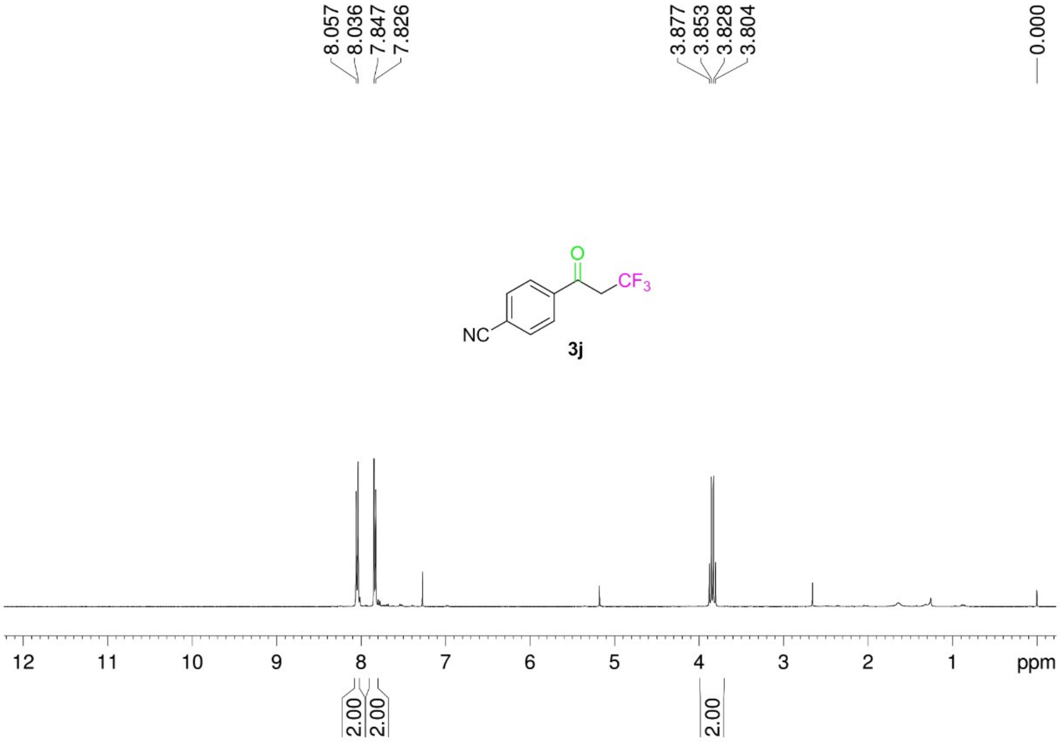
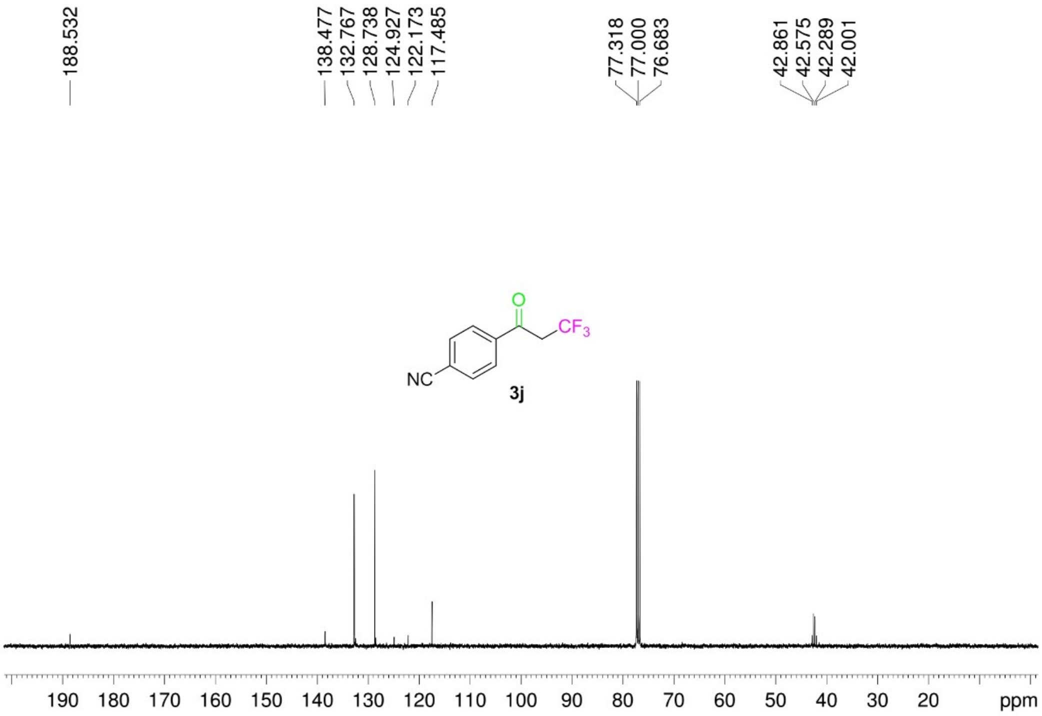
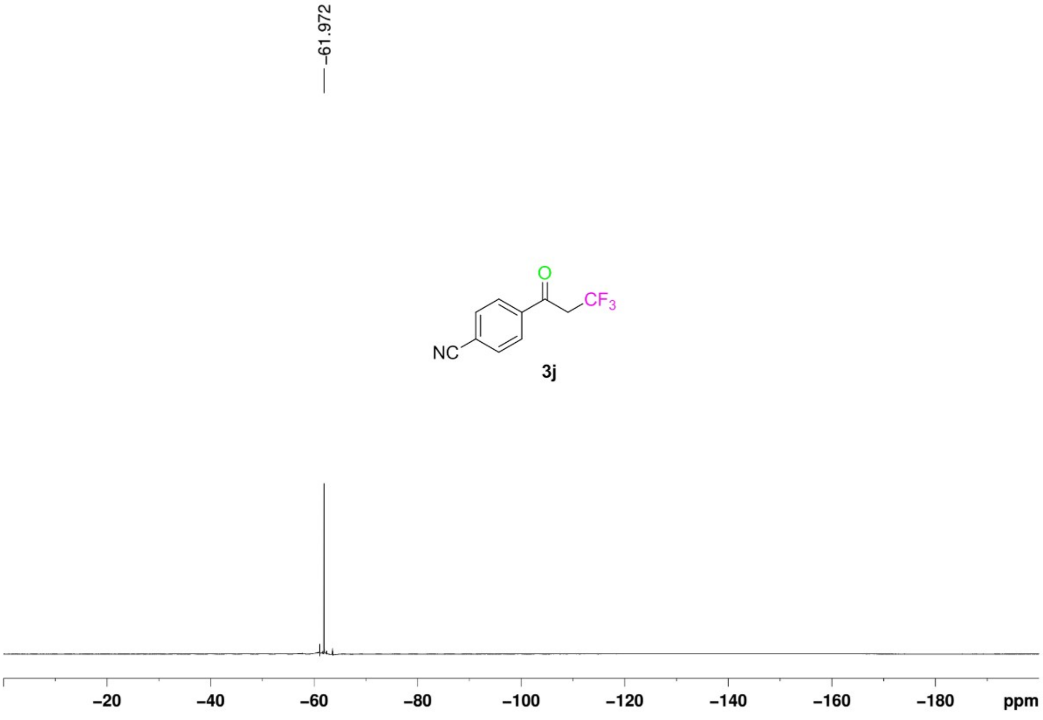
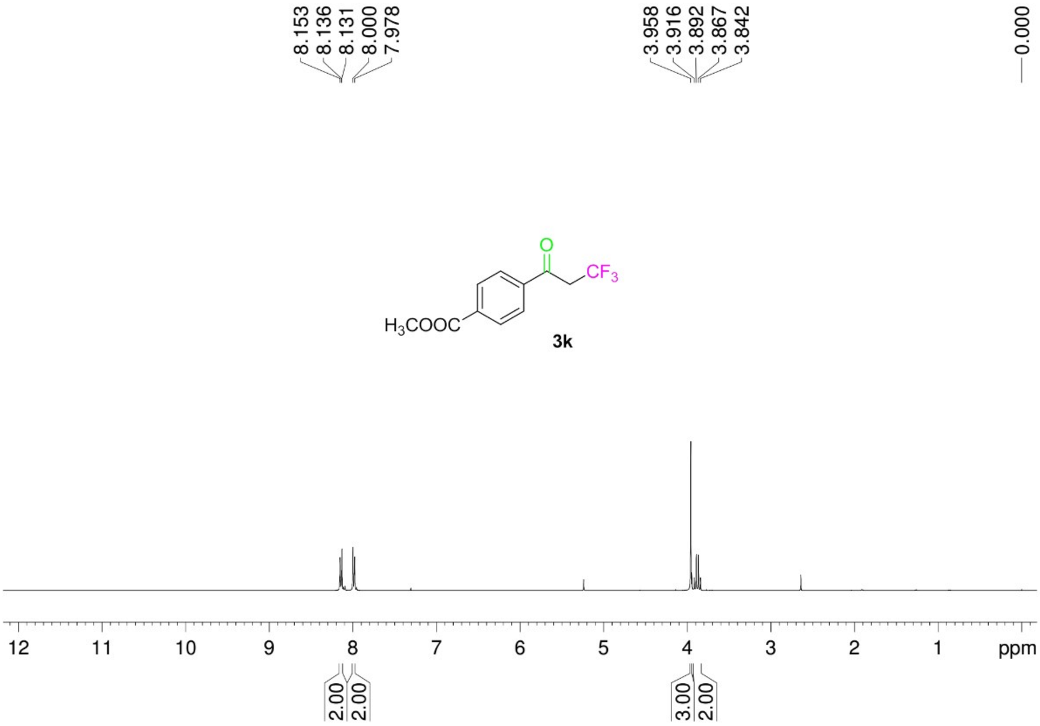
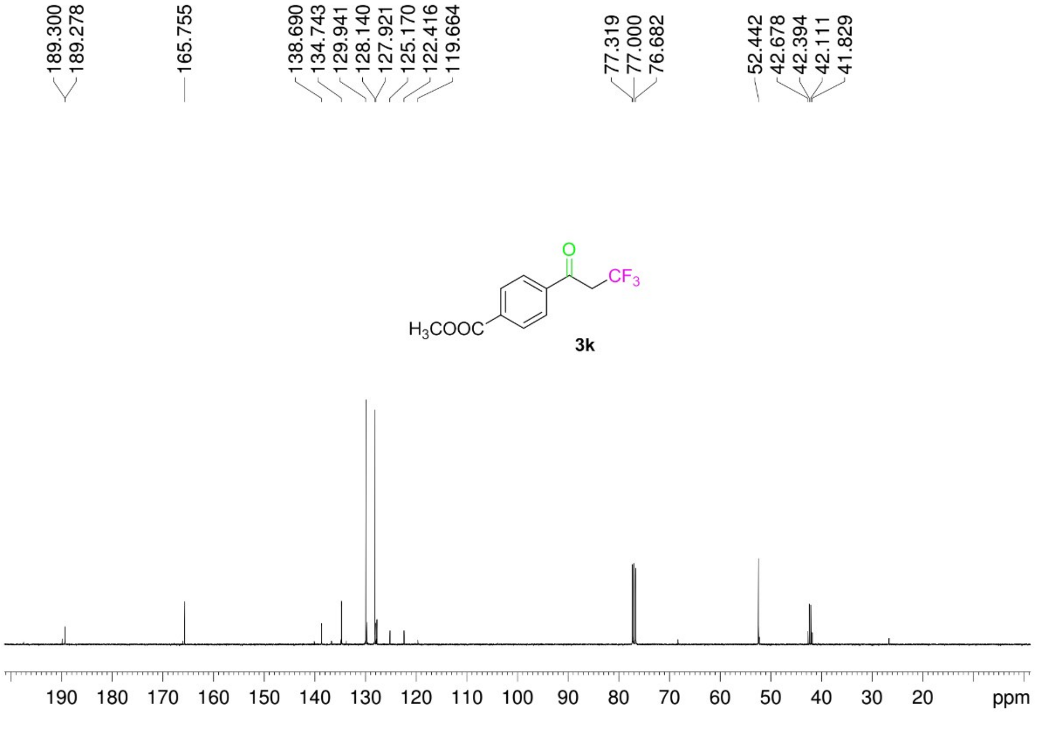
Ph
3i
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

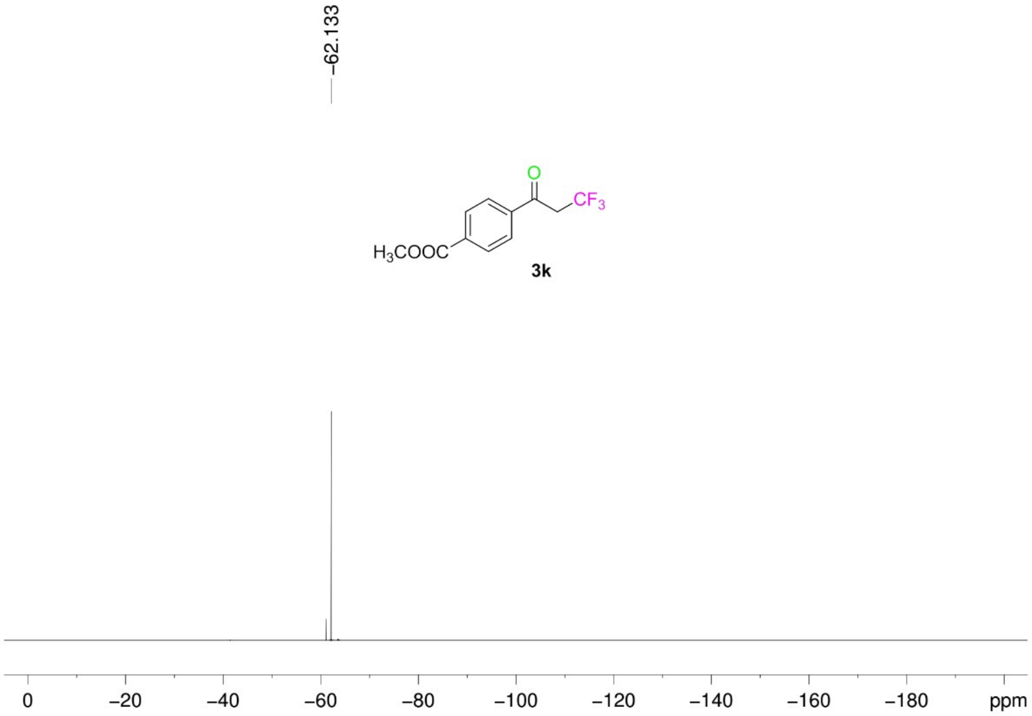

8.057
8.036
7.847
7.826
3.877
3.853
3.828
3.804
0.000
O
CF3
NC
3j
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
2.00


188.532
138.477
132.767
128.738
124.927
122.173
117.485
77.318
77.000
76.683
42.861
42.575
42.289
42.001
O
CF$_3$
NC
3j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

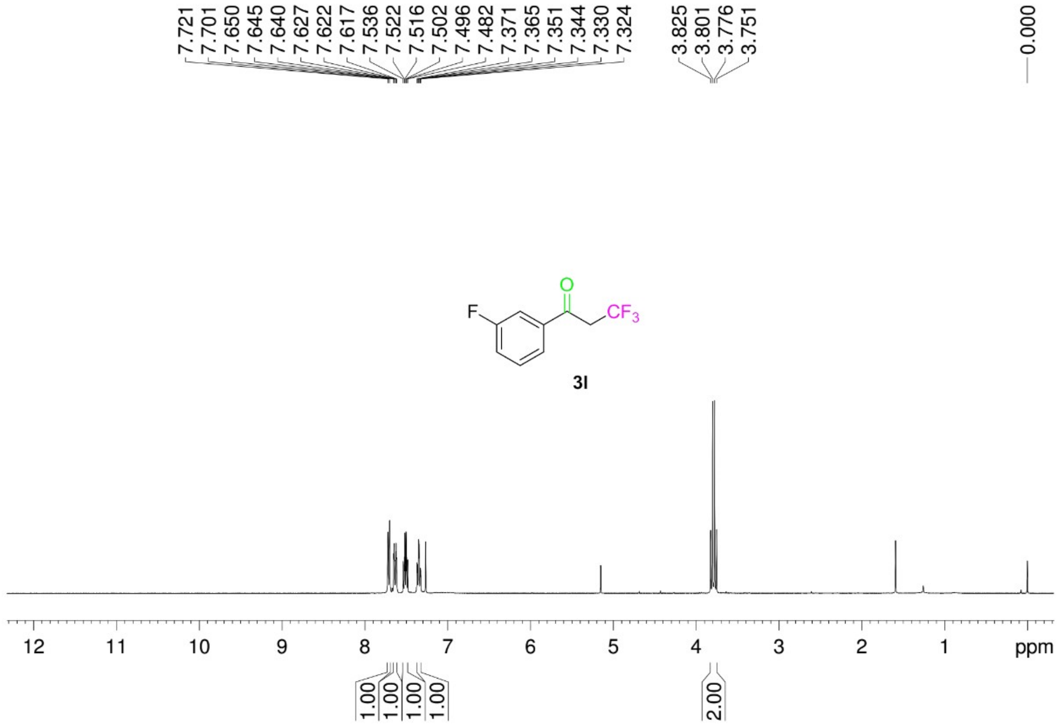

-61.972
O
CF$_3$
NC
3j
-20 -40 -60 -80 -100 -120 -140 -160 -180
ppm


8.153
8.136
8.131
8.000
7.978
3.958
3.916
3.892
3.867
3.842
0.000
O
CF3
H3COOC
3k
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
3.00
2.00


189.300
189.278
165.755
138.690
134.743
129.941
128.140
127.921
125.170
122.416
119.664
77.319
77.000
76.682
52.442
42.678
42.394
42.111
41.829
O
CF3
H3COOC
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


−62.133
O
CF3
H3COOC
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

3k


7.721
7.701
7.650
7.645
7.640
7.627
7.622
7.617
7.536
7.522
7.516
7.502
7.496
7.482
7.371
7.365
7.351
7.344
7.330
7.324
3.825
3.801
3.776
3.751
0.000
F
O
CF3
12
11
10
9
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5
4
3
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ppm
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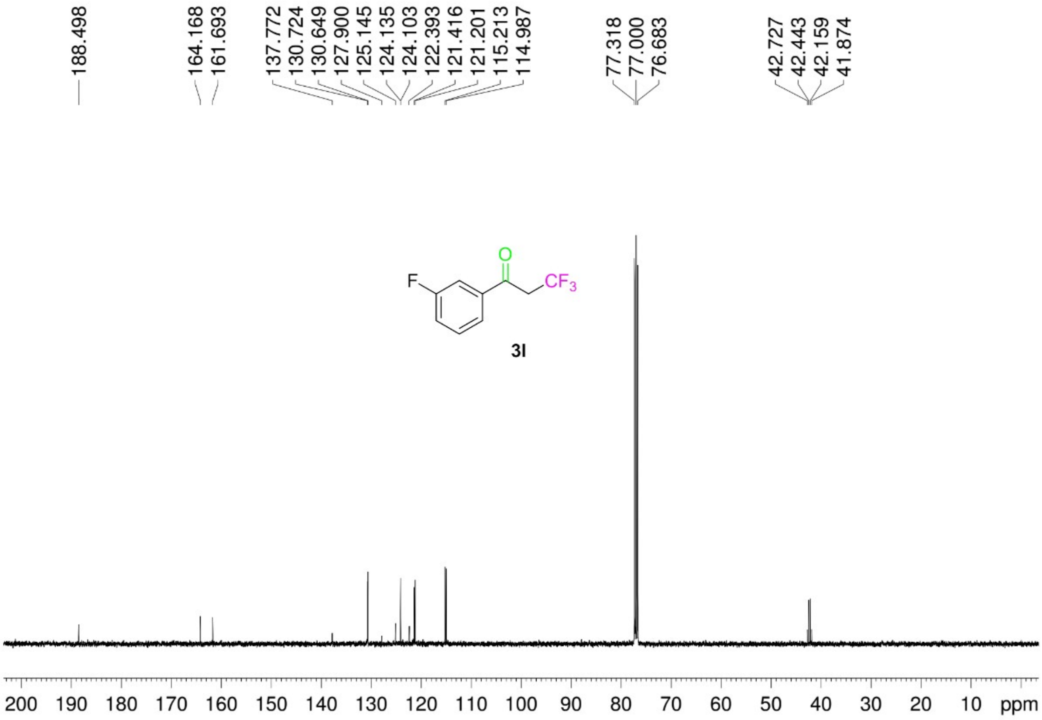
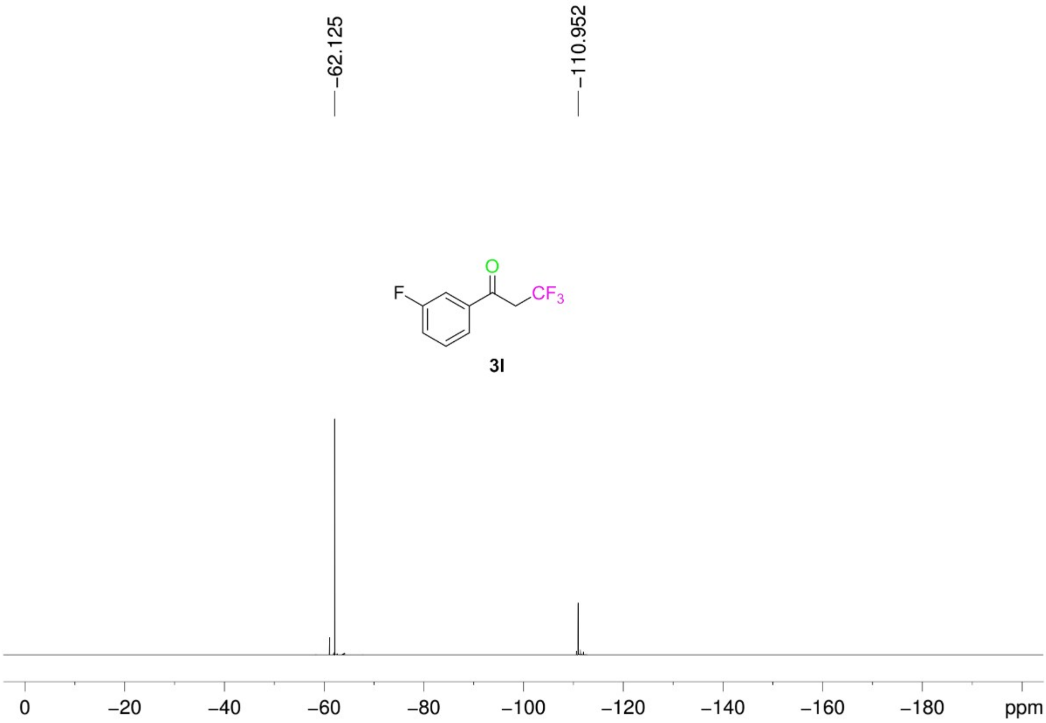
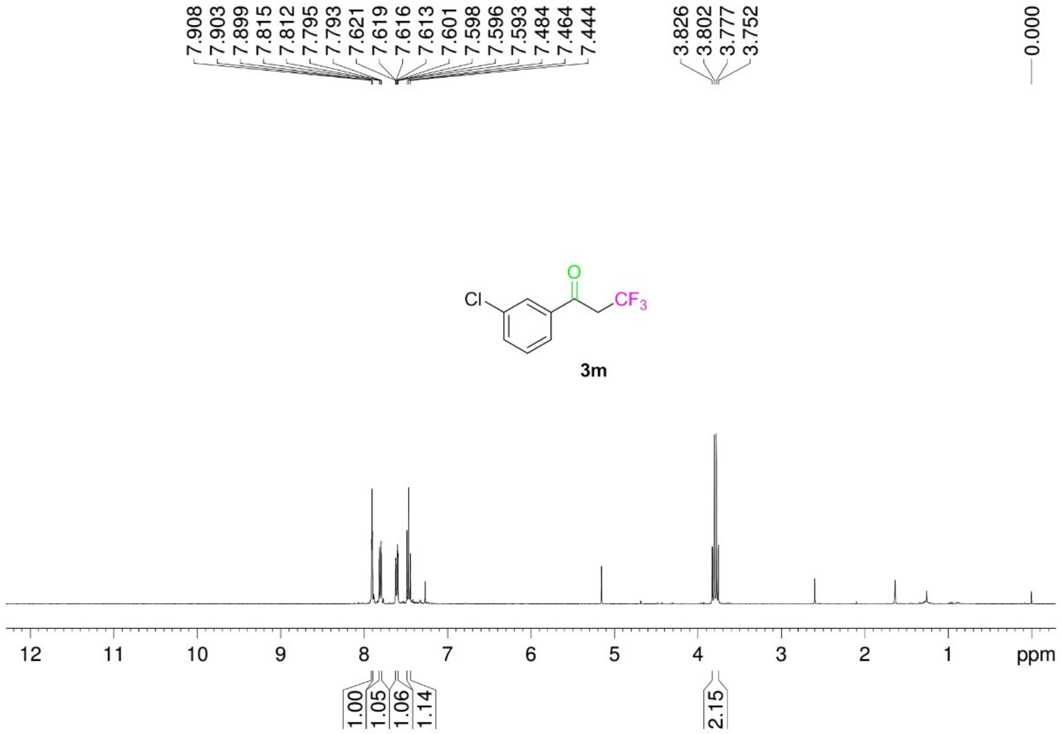
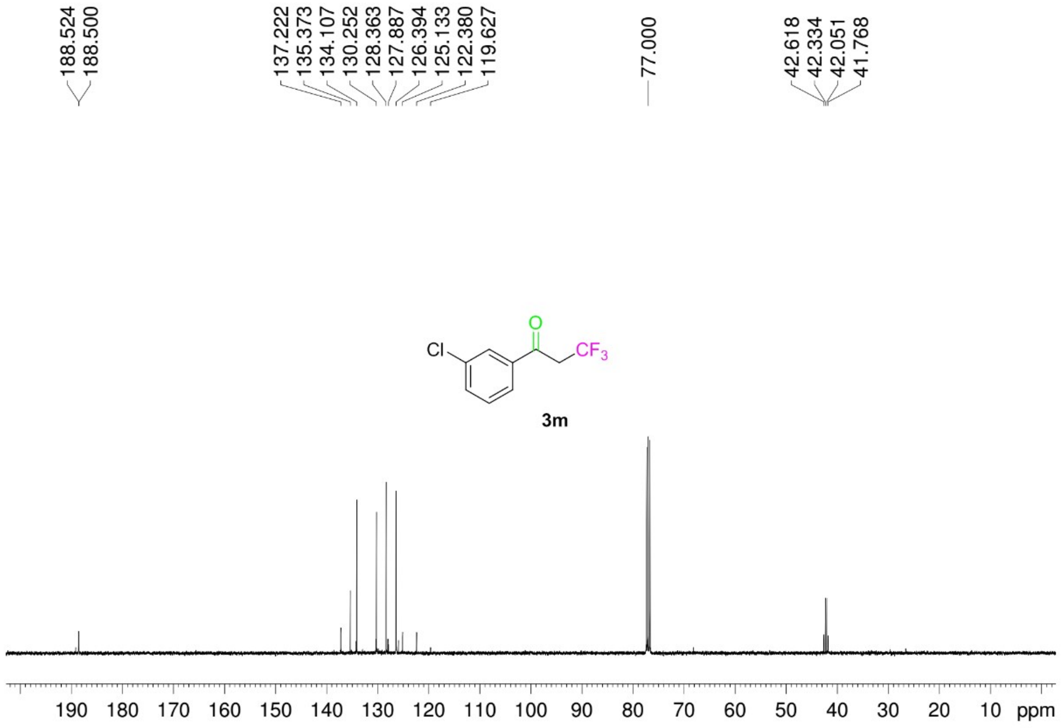
1.00
1.00
2.00

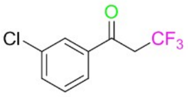
3l


188.498
164.168
161.693
137.772
130.724
130.649
127.900
125.145
124.135
124.103
122.393
121.416
121.201
115.213
114.987
77.318
77.000
76.683
42.727
42.443
42.159
41.874
F
O
CF3
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

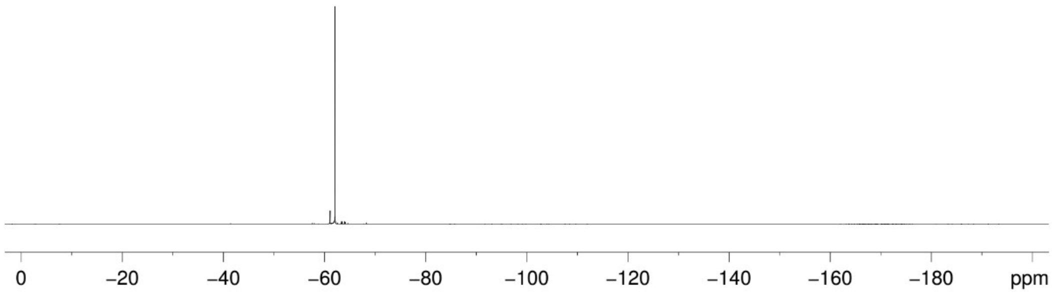

−62.125
−110.952
F
O
CF3
3l
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 ppm


7.908
7.903
7.899
7.815
7.812
7.795
7.793
7.621
7.619
7.616
7.613
7.601
7.598
7.596
7.593
7.484
7.464
7.444
3.826
3.802
3.777
3.752
0.000
Cl
O
CF3
3m
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
1.06
1.14
2.15


188.524
188.500
137.222
135.373
134.107
130.252
128.363
127.887
126.394
125.133
122.380
119.627
77.000
42.618
42.334
42.051
41.768
Cl
O
CF3
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



3m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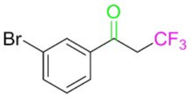
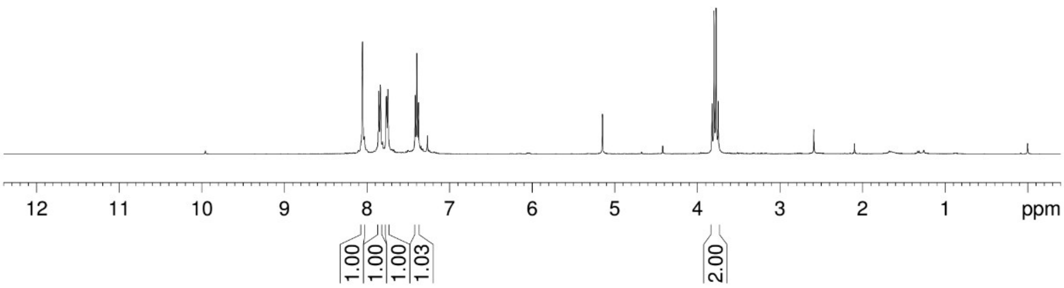
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm



3n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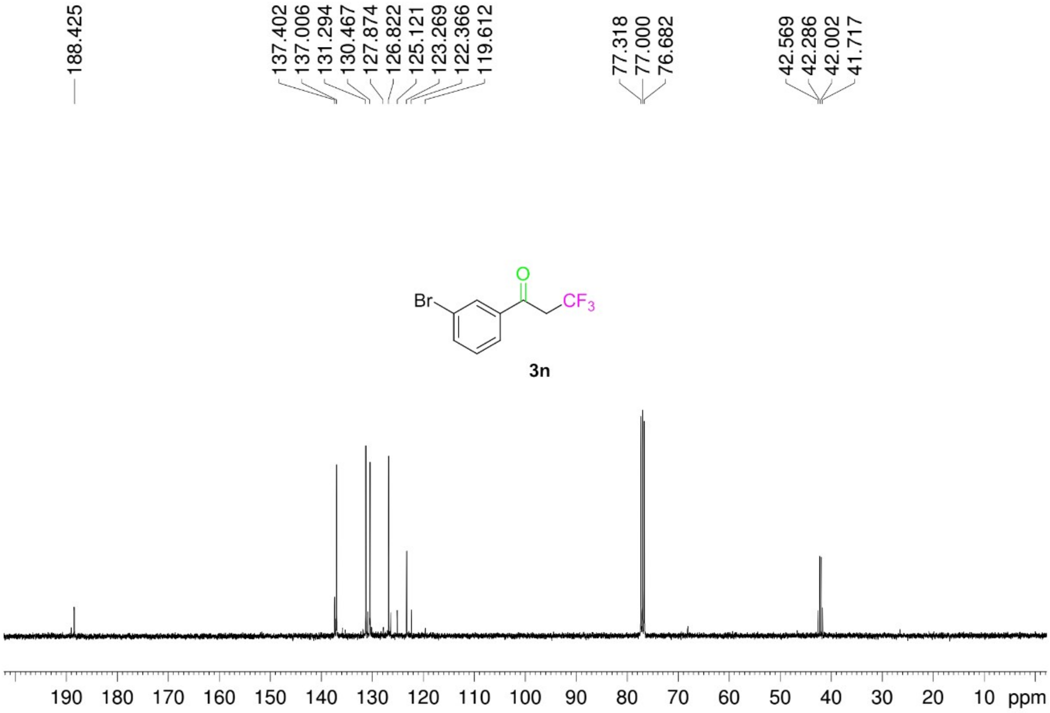
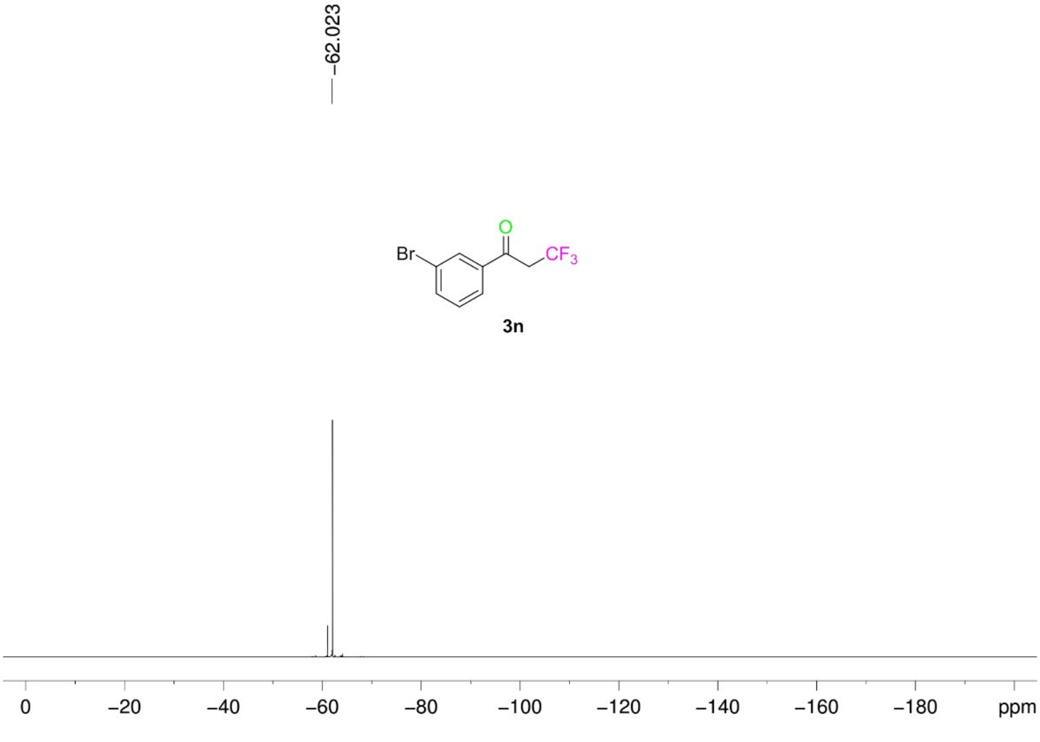
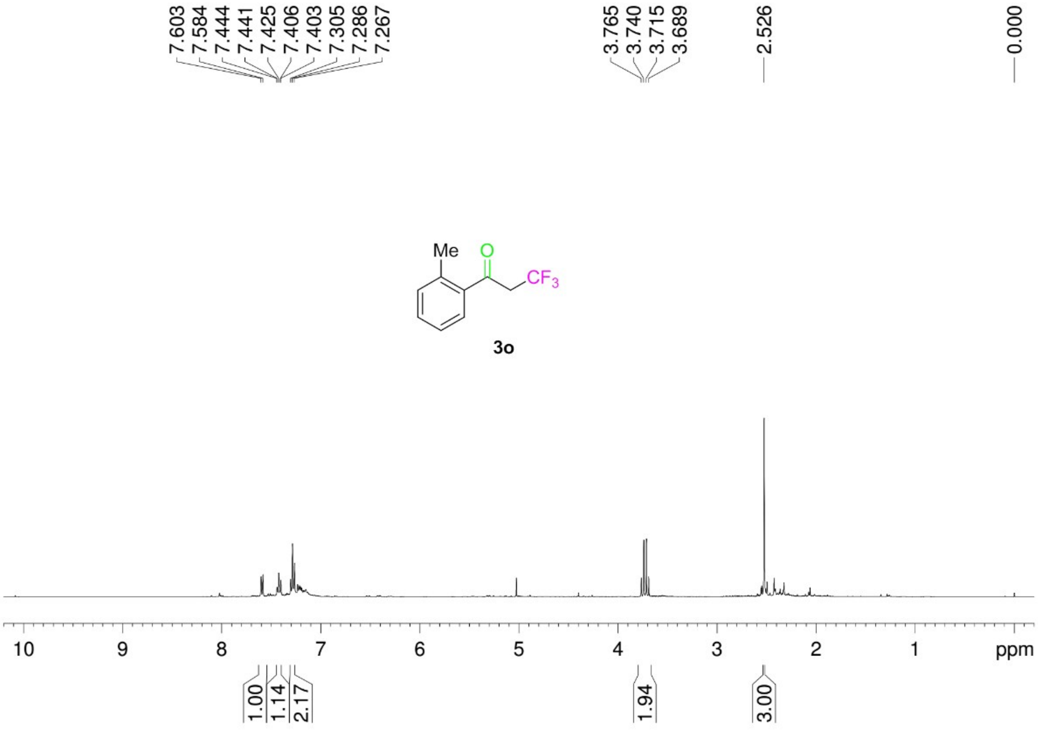
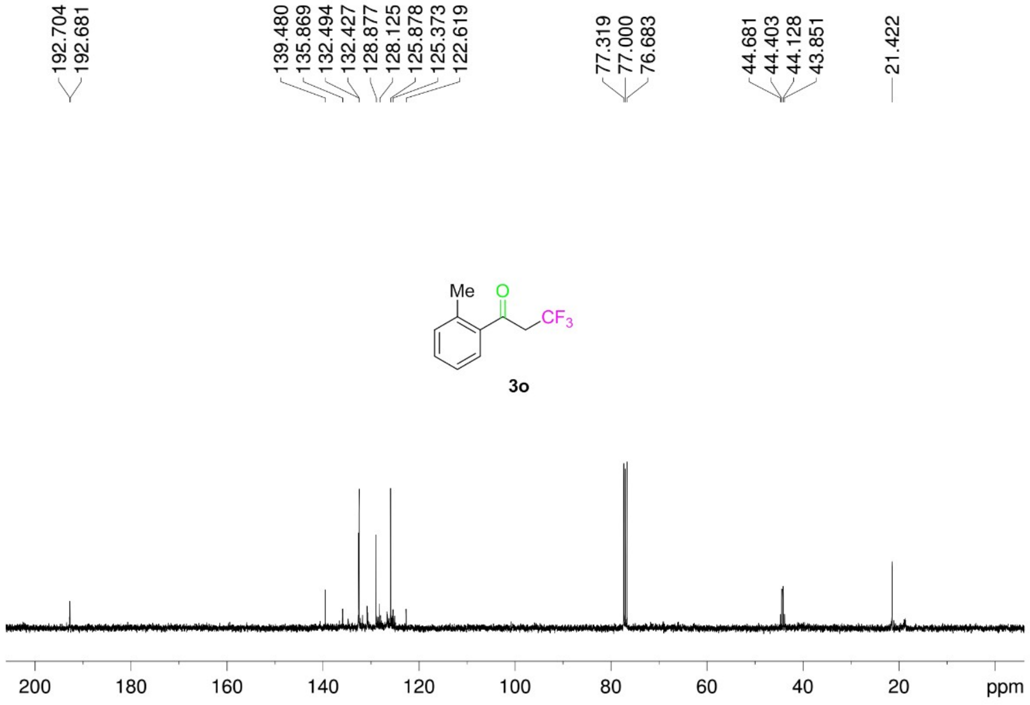
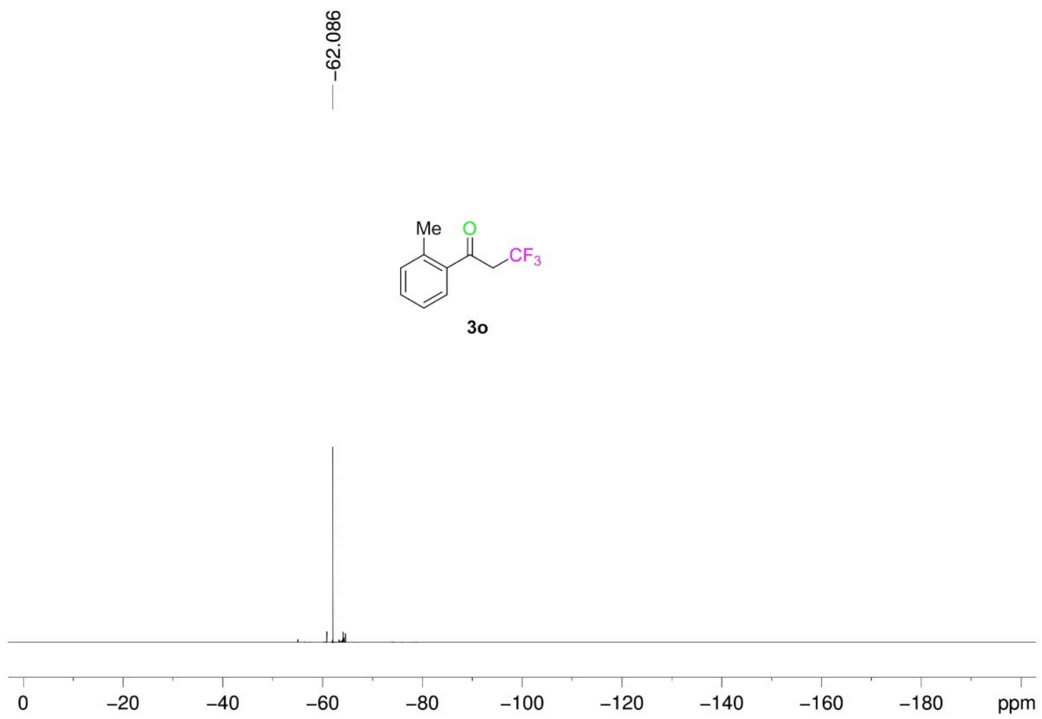
7.857
7.838
7.766
7.746
7.416
7.396
7.377
3.821
3.796
3.771
3.747
0.000
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.03
2.00


188.425
137.402
137.006
131.294
130.467
127.874
126.822
125.121
123.269
122.366
119.612
77.318
77.000
76.682
42.569
42.286
42.002
41.717
Br
O
CF3
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


−62.023
Br
O
CF3
3n
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 ppm


7.603
7.584
7.444
7.441
7.425
7.406
7.403
7.305
7.286
7.267
3.765
3.740
3.715
3.689
2.526
0.000
Me
O
CF$_3$
3o
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.14
2.17
1.94
3.00


192.704
192.681
139.480
135.869
132.494
132.427
128.877
128.125
125.878
125.373
122.619
77.319
77.000
76.683
44.681
44.403
44.128
43.851
21.422
Me
O
CF$_3$
3o
200
180
160
140
120
100
80
60
40
20
ppm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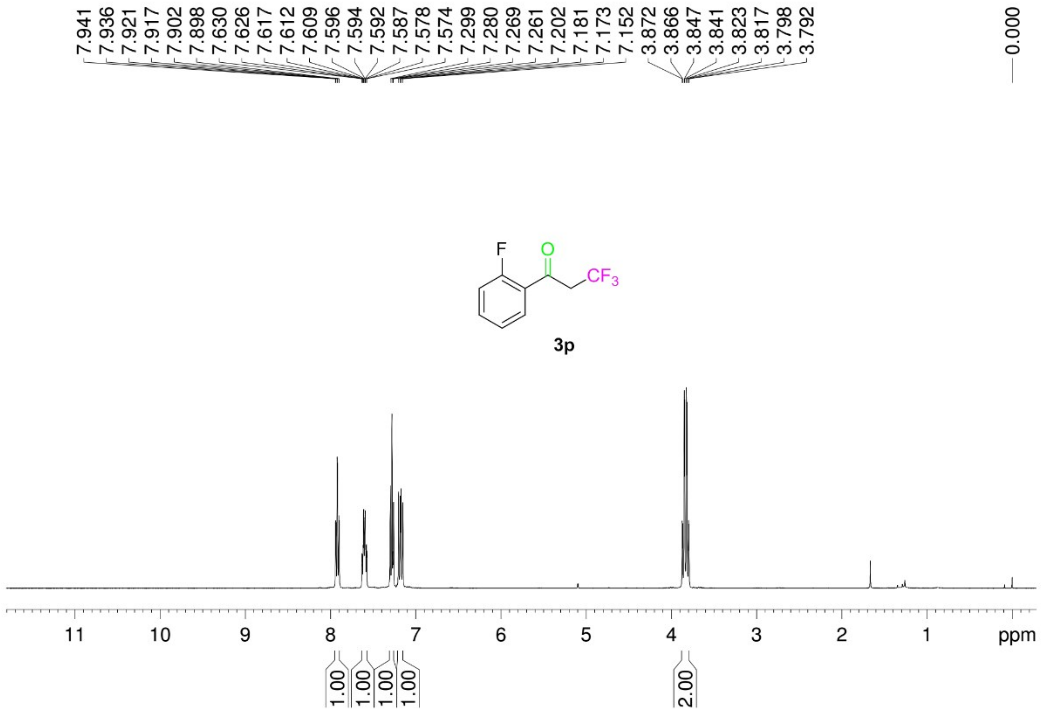
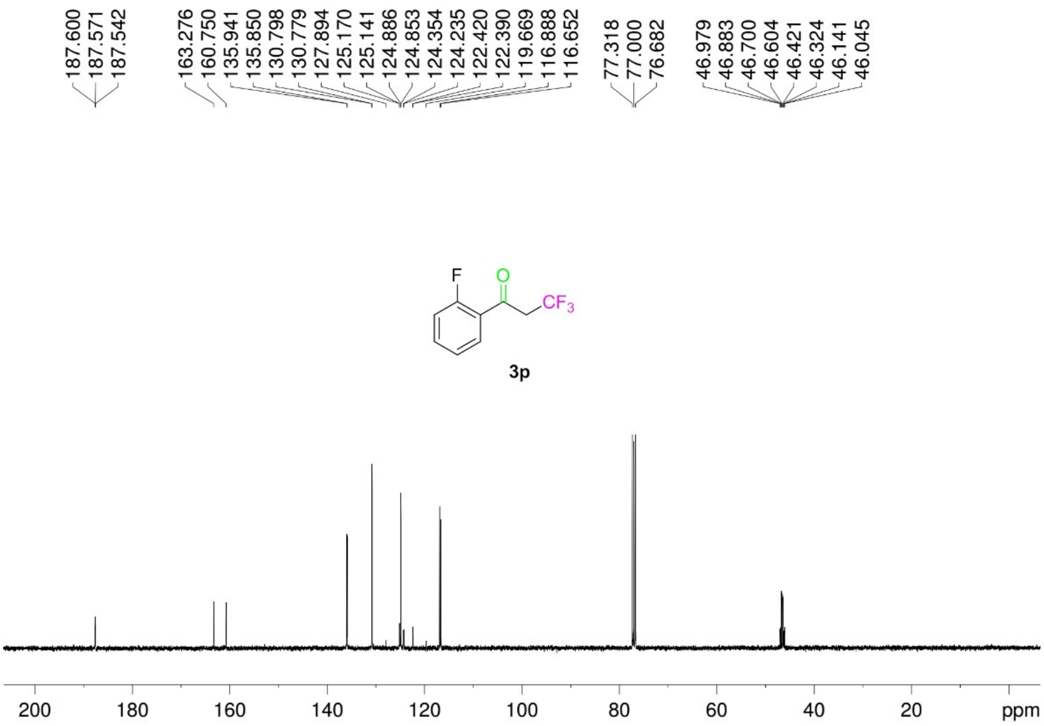
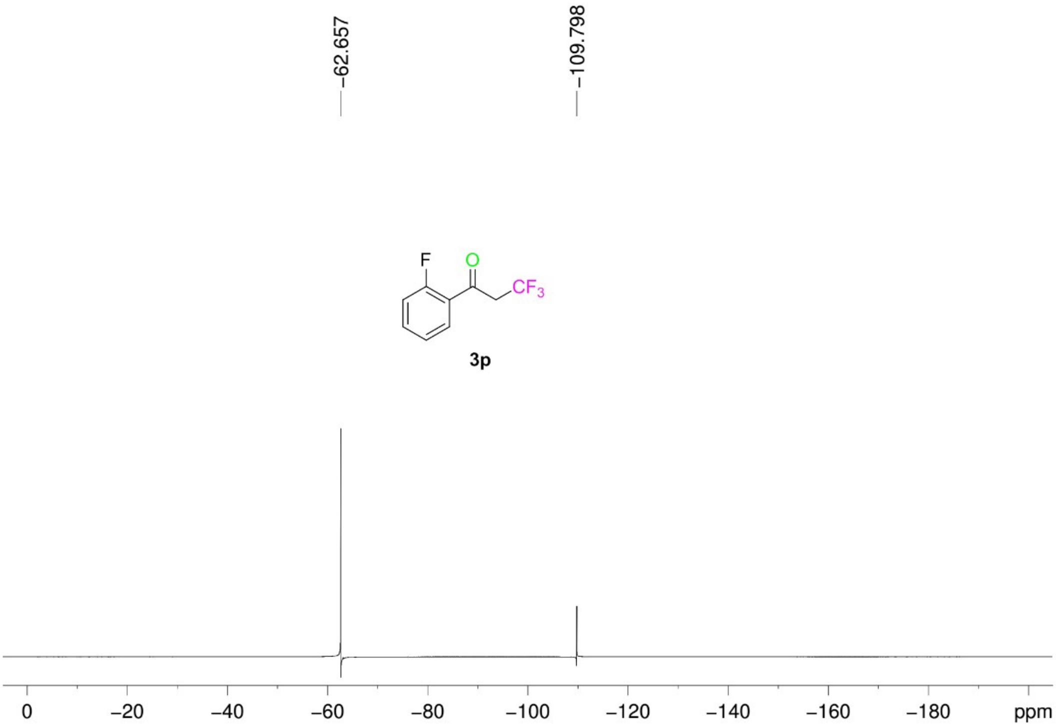
Me
O
CF3
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

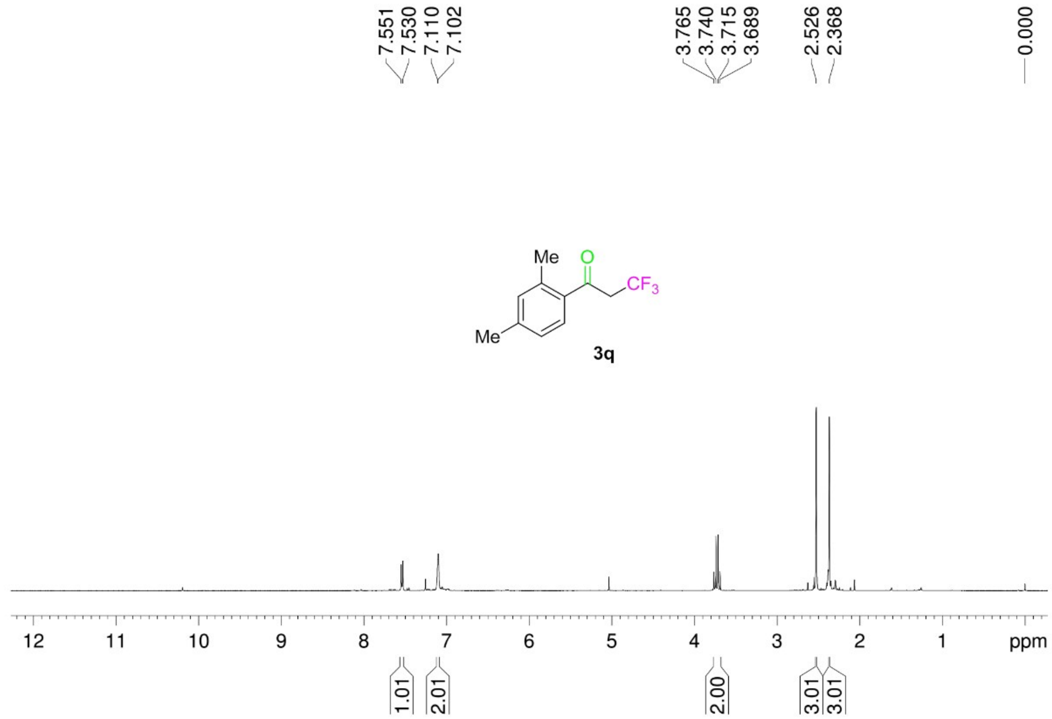
3o

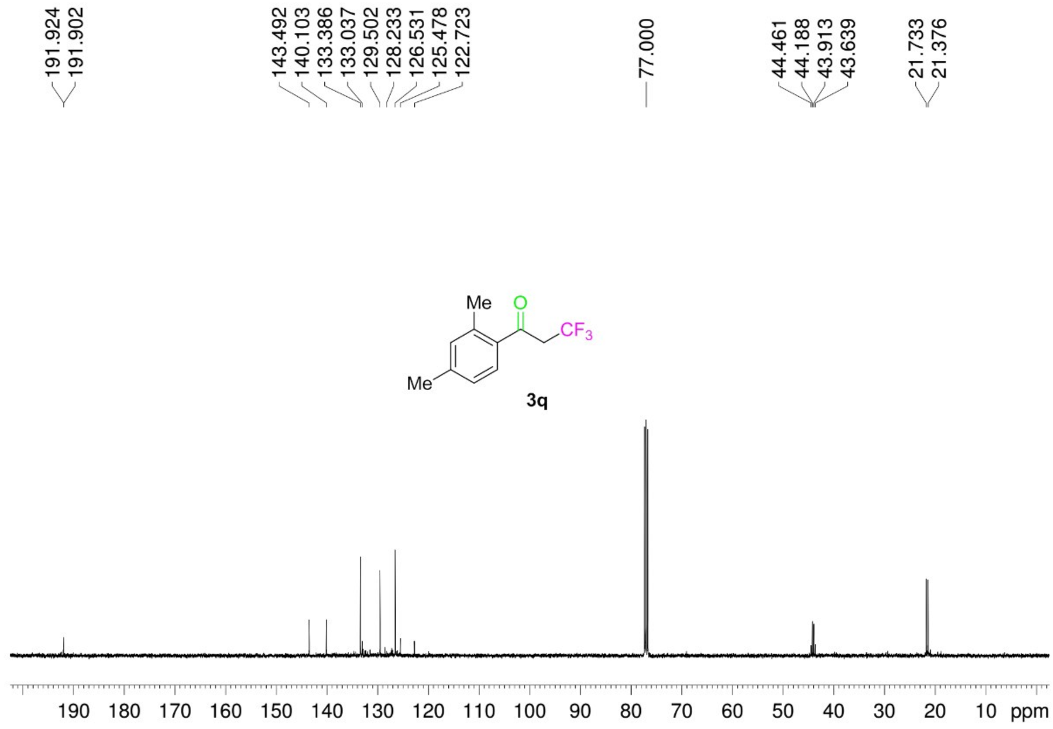

7.941
7.936
7.921
7.917
7.902
7.898
7.630
7.626
7.617
7.612
7.609
7.596
7.594
7.592
7.587
7.578
7.574
7.299
7.280
7.269
7.261
7.202
7.181
7.173
7.152
3.872
3.866
3.847
3.841
3.823
3.817
3.798
3.792
0.000
F
O
CF3
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
2.00

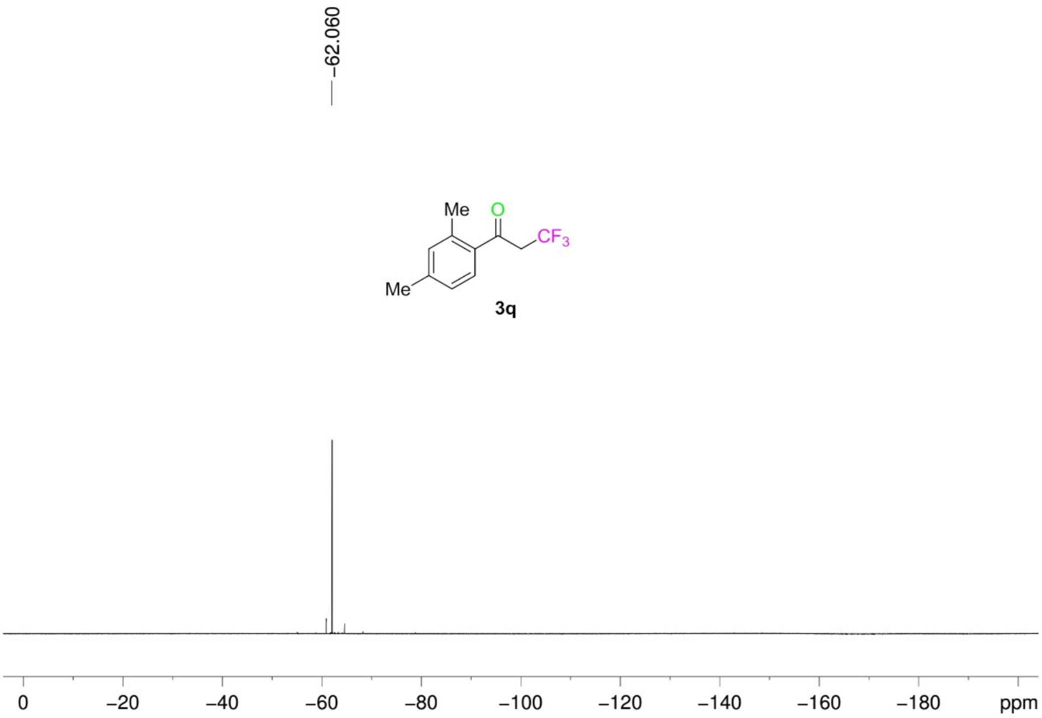
3p

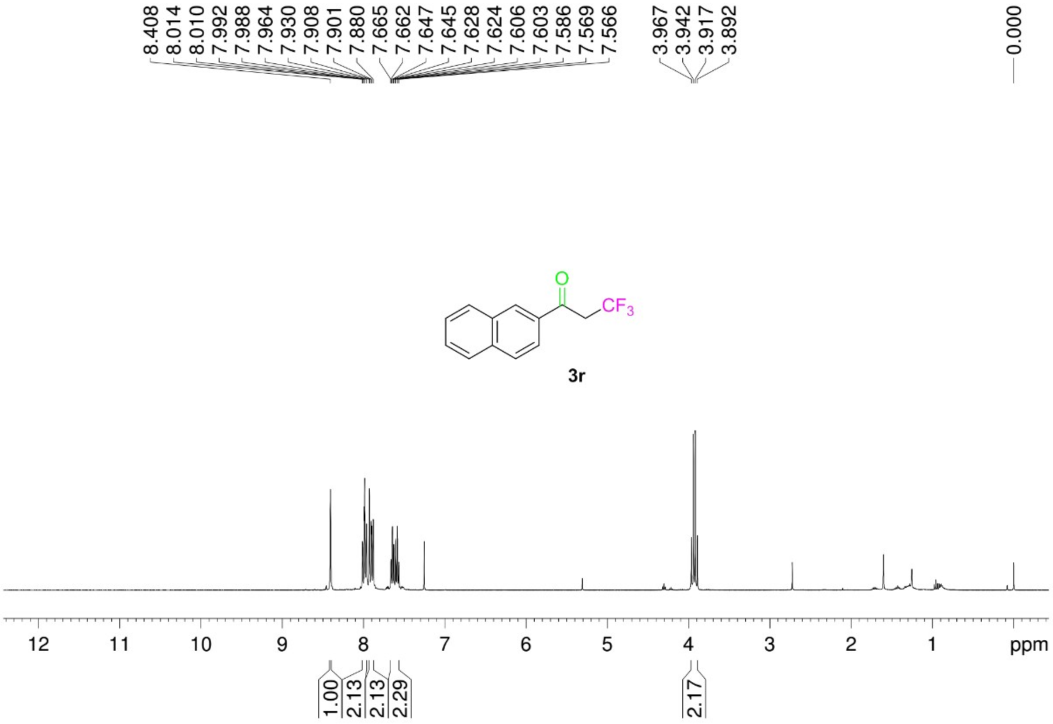

187.600
187.571
187.542
163.276
160.750
135.941
135.850
130.798
130.779
127.894
125.170
125.141
124.886
124.853
124.354
124.235
122.420
122.390
119.669
116.888
116.652
77.318
77.000
76.682
46.979
46.883
46.700
46.604
46.421
46.324
46.141
46.045
F
O
CF3
3p
200
180
160
140
120
100
80
60
40
20
ppm

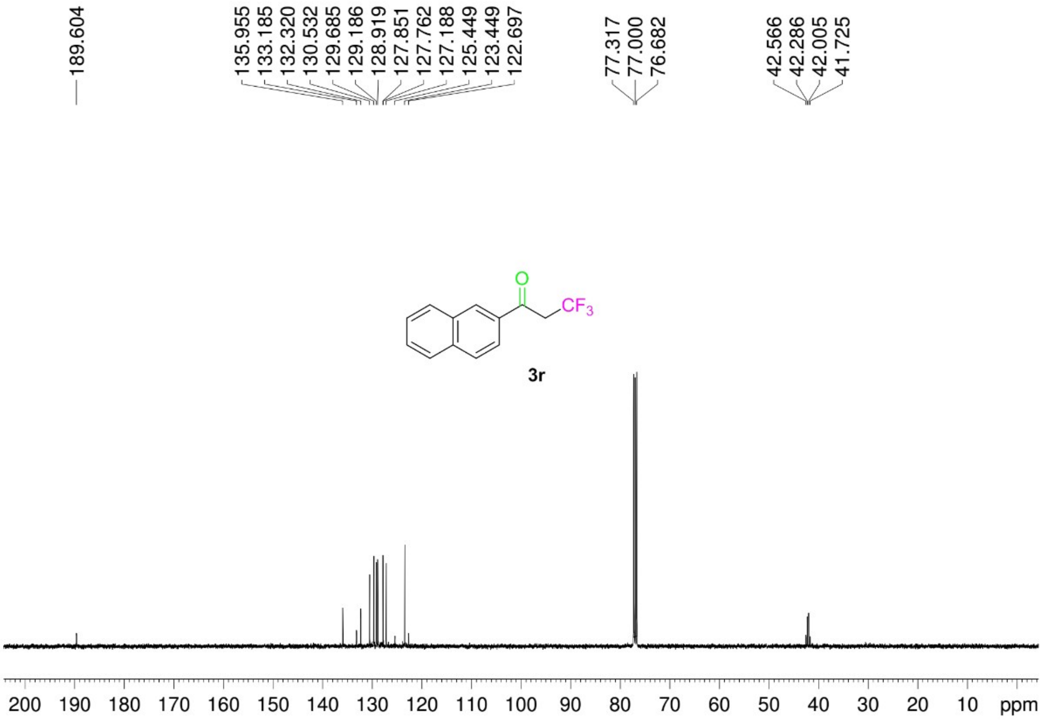

−62.657
−109.798
F
O
CF3
3p
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

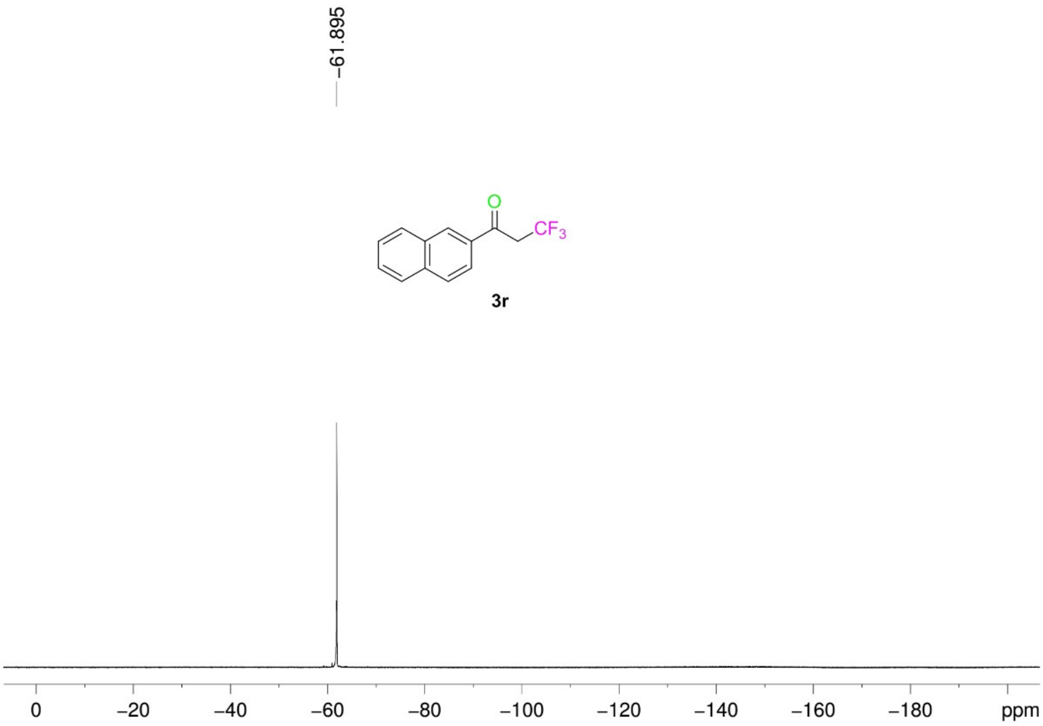

7.551
7.530
7.110
7.102
3.765
3.740
3.715
3.689
2.526
2.368
0.000
Me
O
CF3
Me
3q
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
2.01
2.00
3.01
3.01

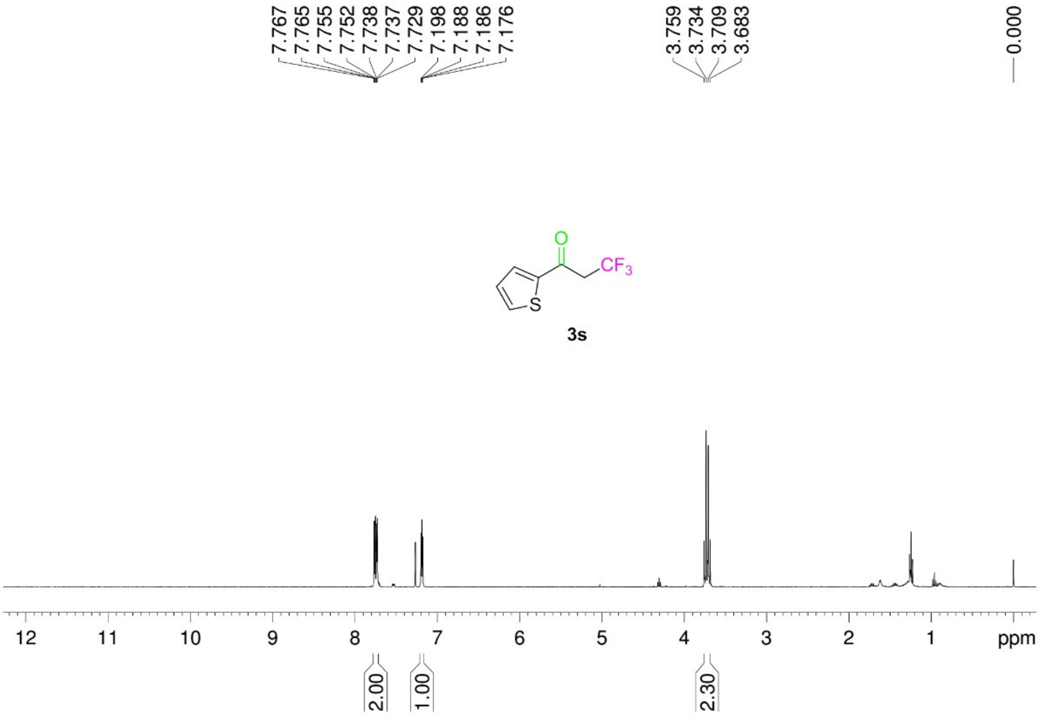

191.924
191.902
143.492
140.103
133.386
133.037
129.502
128.233
126.531
125.478
122.723
77.000
44.461
44.188
43.913
43.639
21.733
21.376
Me
O
CF3
Me
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

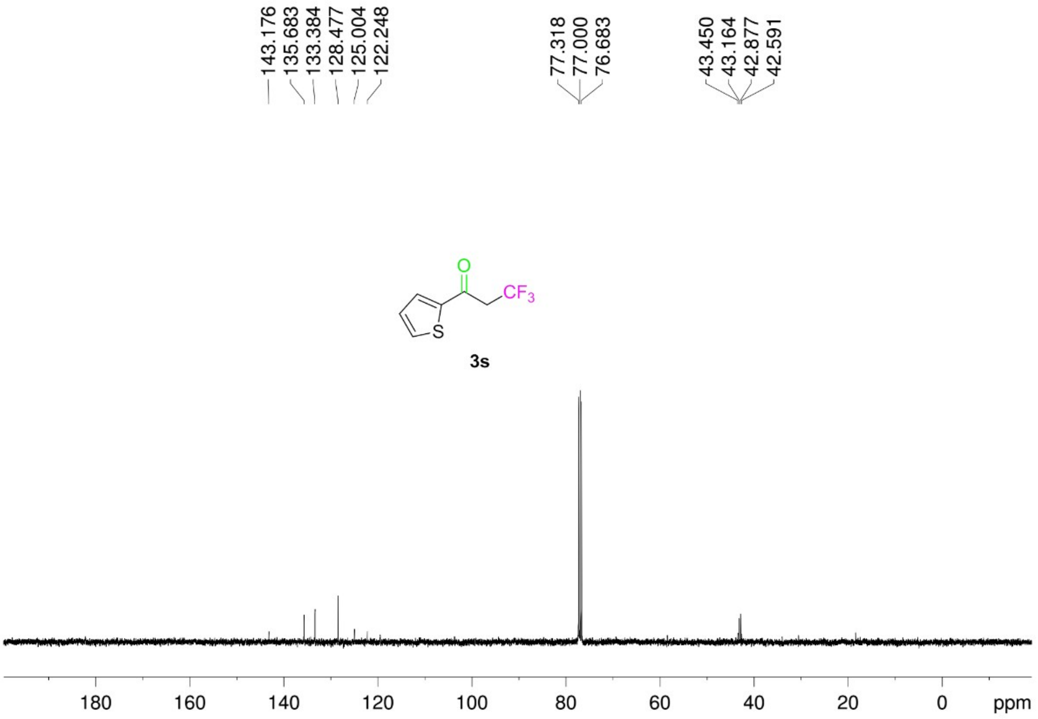

−62.060
Me
O
CF3
Me
3q
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

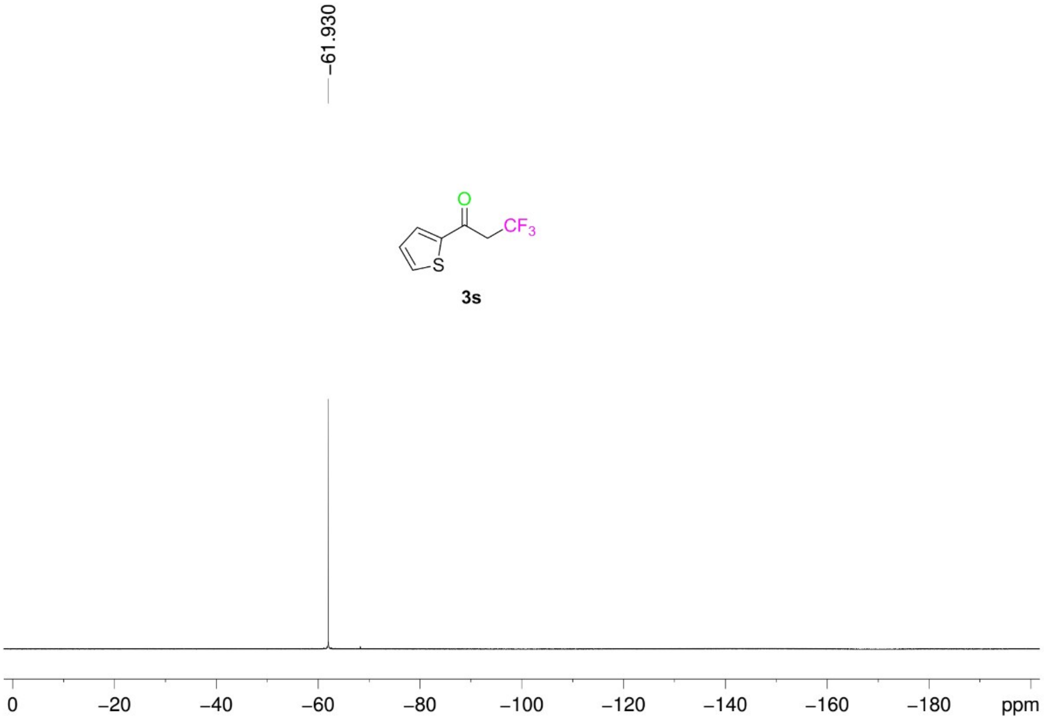

8.408
8.014
8.010
7.992
7.988
7.964
7.930
7.908
7.901
7.880
7.665
7.662
7.647
7.645
7.628
7.624
7.606
7.603
7.586
7.569
7.566
3.967
3.942
3.917
3.892
0.000
O
CF3
3r
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.13
2.13
2.29
2.17


189.604
135.955
133.185
132.320
130.532
129.685
129.186
128.919
127.851
127.762
127.188
125.449
123.449
122.697
77.317
77.000
76.682
42.566
42.286
42.005
41.725
O
CF3
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


−61.895
O
CF3
3r
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 ppm

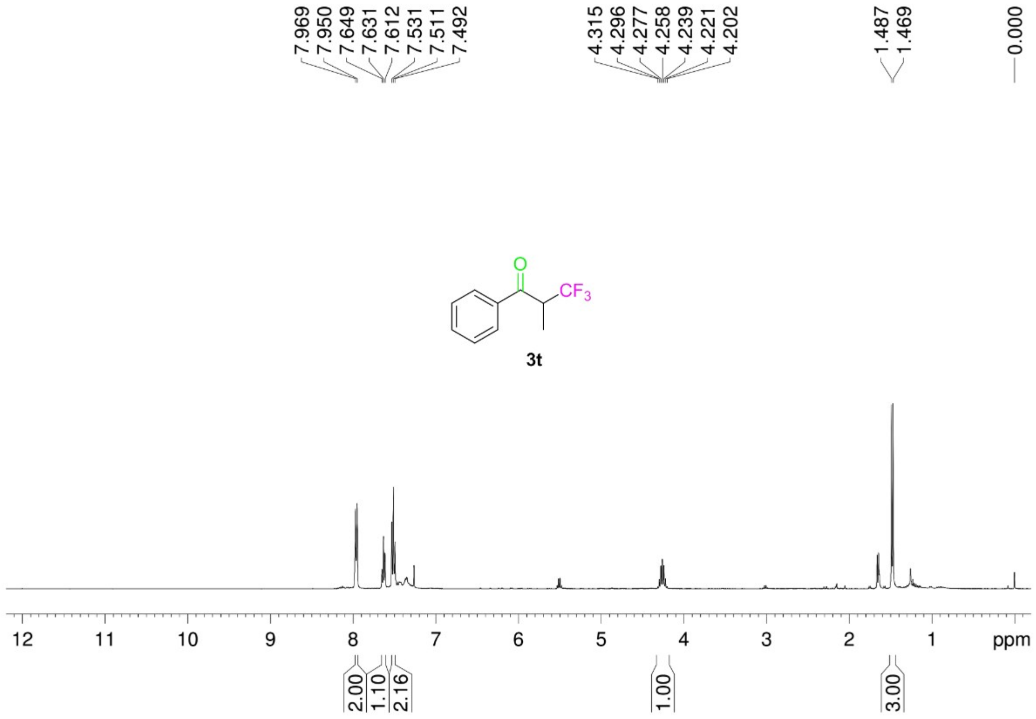

7.767
7.765
7.755
7.752
7.738
7.737
7.729
7.198
7.188
7.186
7.176
3.759
3.734
3.709
3.683
0.000
O
CF3
S
3s
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.00
2.30


143.176
135.683
133.384
128.477
125.004
122.248
77.318
77.000
76.683
43.450
43.164
42.877
42.591
O
CF3
S
3s
180
160
140
120
100
80
60
40
20
0
ppm



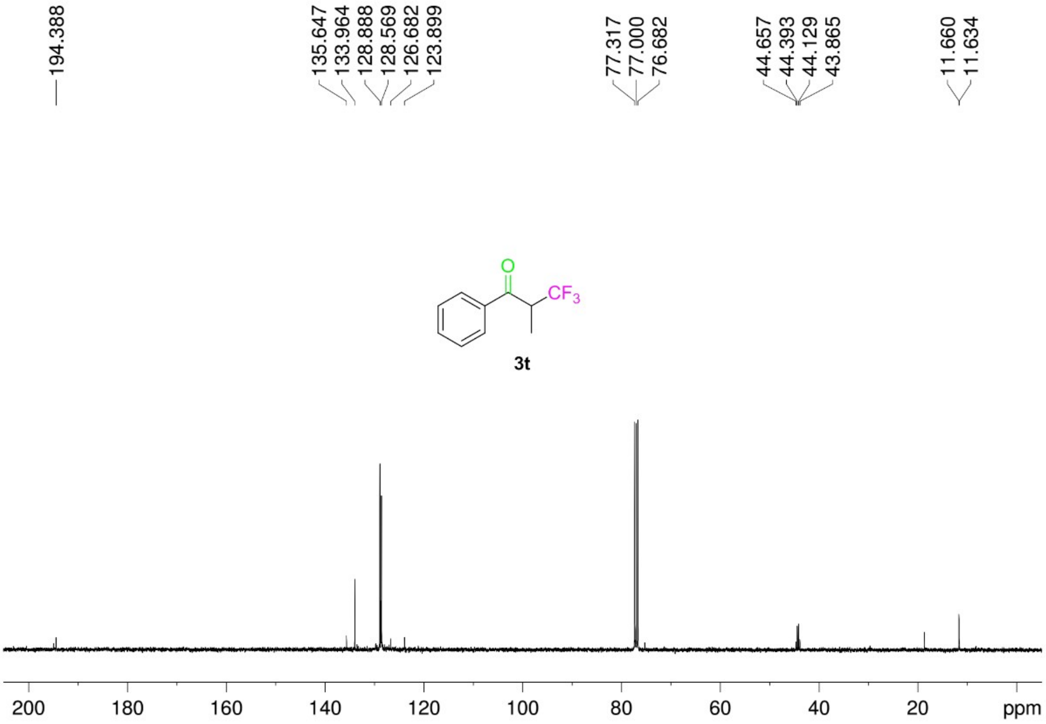
3s

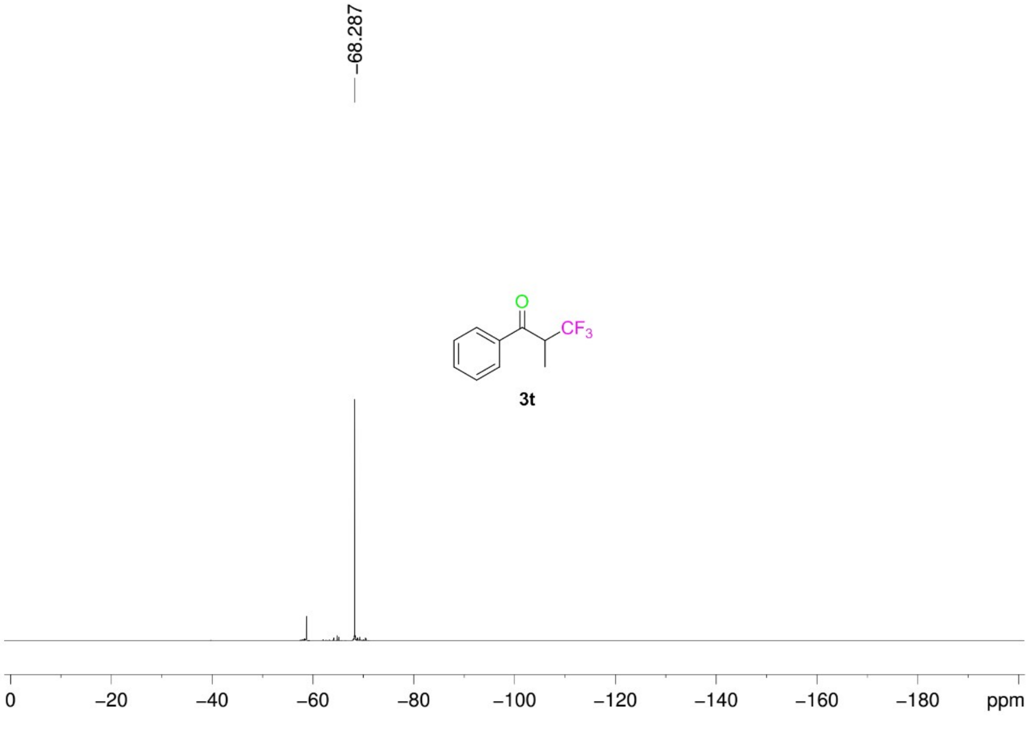
−61.930
O
CF3
S
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm



3t

7.969
7.950
7.649
7.631
7.612
7.531
7.511
7.492
4.315
4.296
4.277
4.258
4.239
4.221
4.202
1.487
1.469
0.000
O
CF3
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.10
2.16
1.00
3.00


194.388
135.647
133.964
128.888
128.569
126.682
123.899
77.317
77.000
76.682
44.657
44.393
44.129
43.865
11.660
11.634
O
CF3
3t
200
180
160
140
120
100
80
60
40
20
ppm


−68.287
O
CF3
3t
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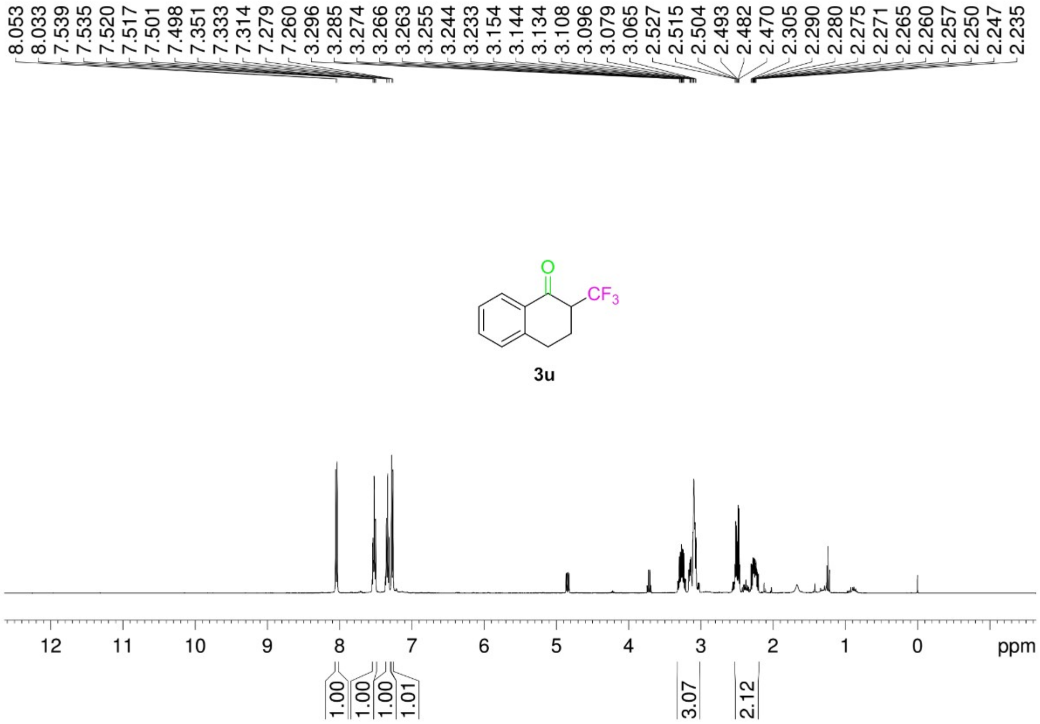
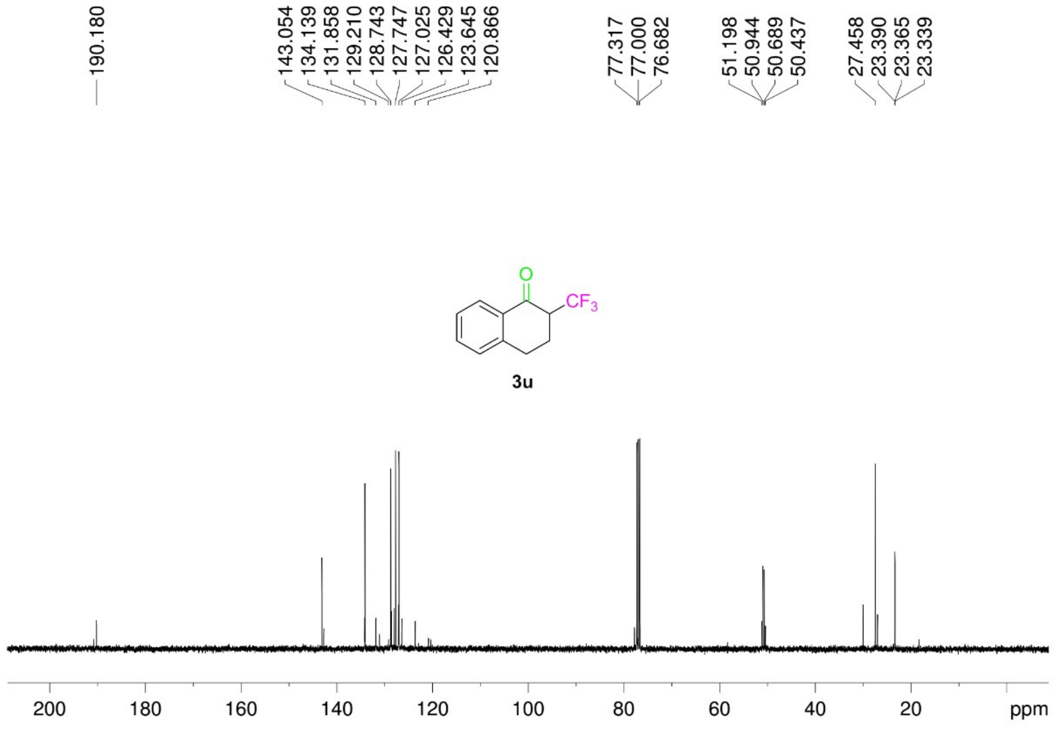
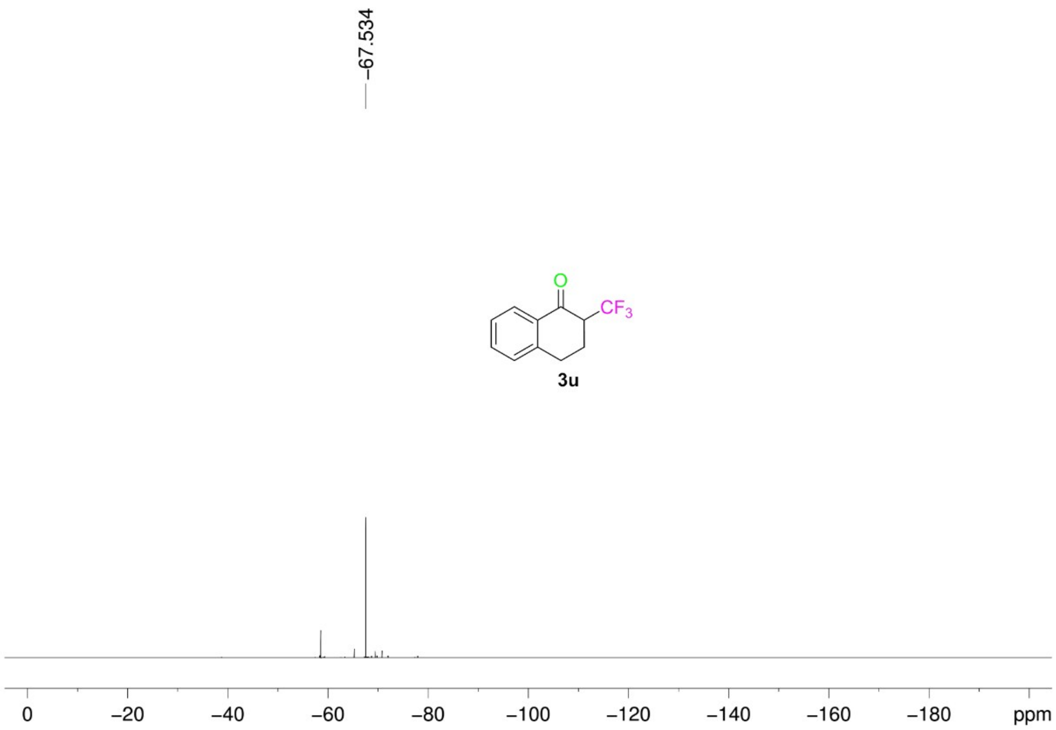
−100
−120
−140
−160
−180
ppm


8.053
8.033
7.539
7.535
7.520
7.517
7.501
7.498
7.351
7.333
7.314
7.279
7.260
3.296
3.285
3.274
3.266
3.263
3.255
3.244
3.233
3.154
3.144
3.134
3.108
3.096
3.079
3.065
2.527
2.515
2.504
2.493
2.482
2.470
2.305
2.290
2.280
2.275
2.271
2.265
2.260
2.257
2.250
2.247
2.235
O
CF3
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
1.01
3.07
2.12

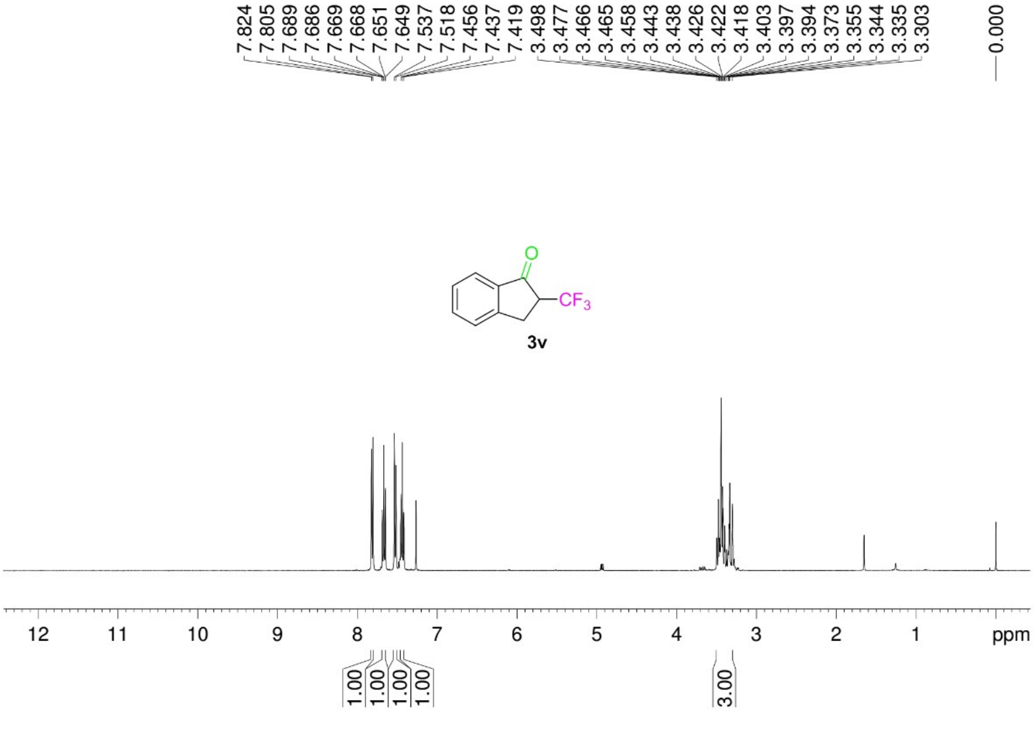
3u


190.180
143.054
134.139
131.858
129.210
128.743
127.747
127.025
126.429
123.645
120.866
77.317
77.000
76.682
51.198
50.944
50.689
50.437
27.458
23.390
23.365
23.339
O
CF3
200
180
160
140
120
100
80
60
40
20
ppm

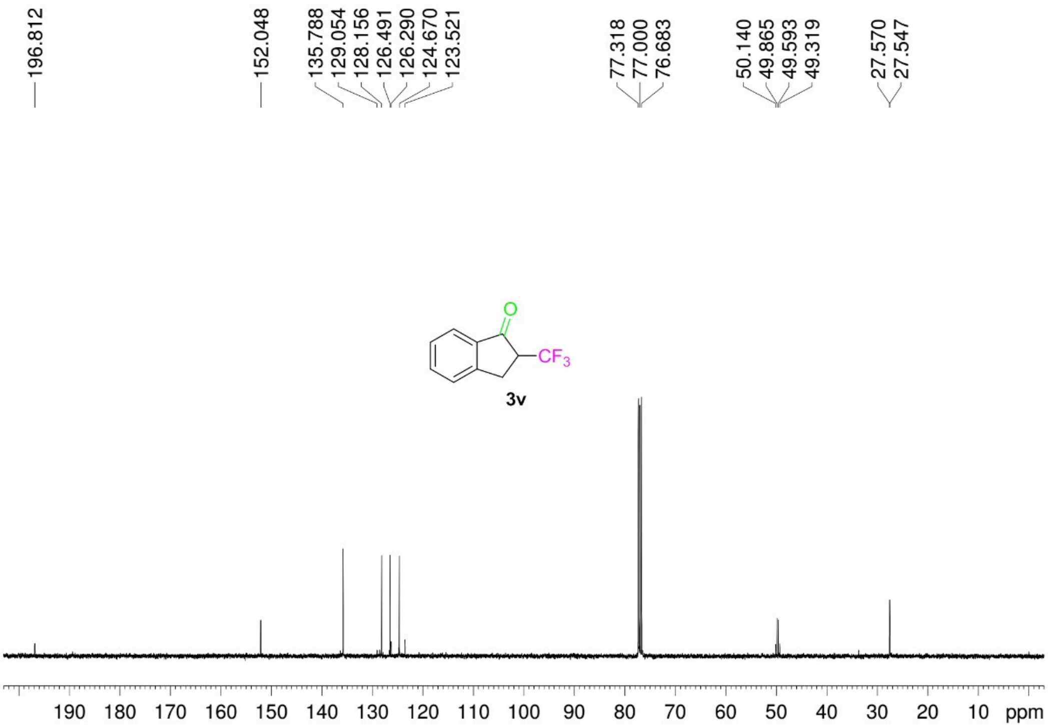
3u

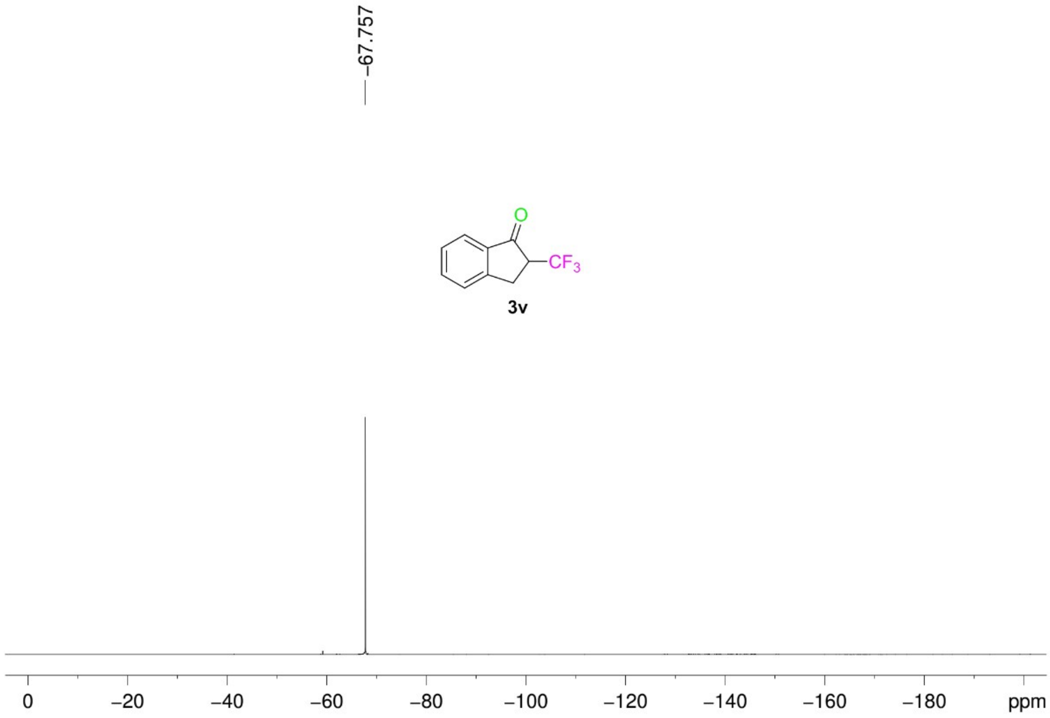

−67.534
O
CF3
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm

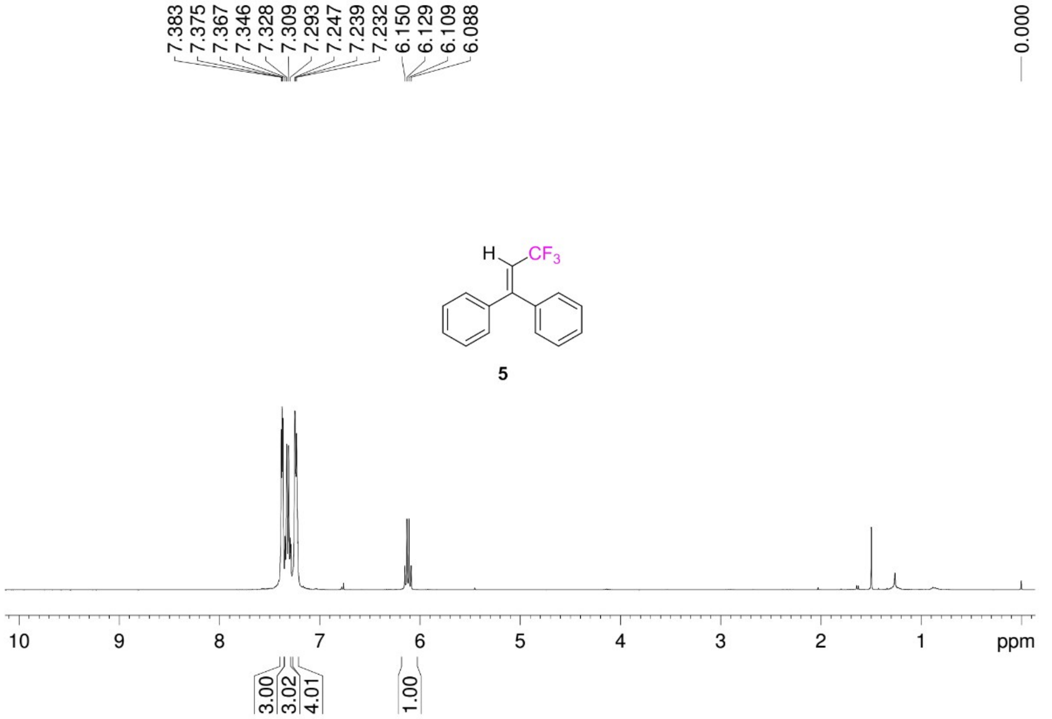
3u

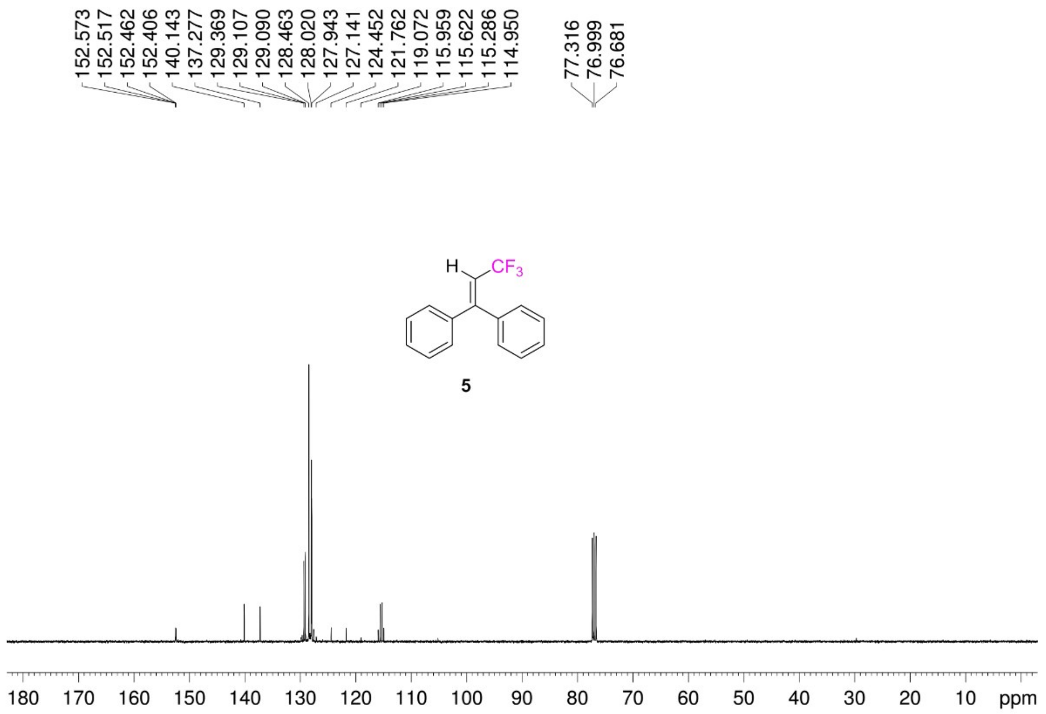

7.824
7.805
7.689
7.686
7.669
7.668
7.651
7.649
7.537
7.518
7.456
7.437
7.419
3.498
3.477
3.466
3.465
3.458
3.443
3.438
3.426
3.422
3.418
3.403
3.397
3.394
3.373
3.355
3.344
3.335
3.303
0.000
O
CF3
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
3.00

3v


196.812
152.048
135.788
129.054
128.156
126.491
126.290
124.670
123.521
77.318
77.000
76.683
50.140
49.865
49.593
49.319
27.570
27.547
O
CF3
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


−67.757
O
CF3
3v
0 −20 −40 −60 −80 −100 −120 −140 −160 −180 ppm


7.383
7.375
7.367
7.346
7.328
7.309
7.293
7.247
7.239
7.232
6.150
6.129
6.109
6.088
0.000
H
CF_3
5
10
9
8
7
6
5
4
3
2
1
ppm
3.00
3.02
4.01
1.00


152.573
152.517
152.462
152.406
140.143
137.277
129.369
129.107
129.090
128.463
128.020
127.943
127.141
124.452
121.762
119.072
115.959
115.622
115.286
114.950
77.316
76.999
76.681
H
CF_3
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


–55.586
H
CF3
5
0
–20
–40
–60
–80
–100
–120
–140
–160
–180
ppm